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# New Polymers

Martin G. Broadhurst, Editor

Institute for Materials Research  
National Bureau of Standards  
Washington, D. C. 20234

October 1975

Final

Prepared for  
**Office of Naval Research**  
**Arlington, Virginia 22044**



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## New Polymers

### Introduction

This report contains manuscripts of talks that were presented at the Annual Program Review of the Office of Naval Research. Part of the program focused on piezoelectric measurements and applications of polymers and those papers were compiled previously in an Interagency Report, NBSIR 75-760. The papers in this present report are concerned with the chemical synthesis and characterization of potentially useful new polymers. Together, these two reports are the final reports from NBS to ONR as prescribed in contract number NAonr-44-75.

Commercial materials are identified in this paper to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards.

# Preparation of Polyorganosiloxanes from Inorganic Mineral Silicates.

B.R. Currell.

Thames Polytechnic,

Wellington Street, London, SE18 6PF.

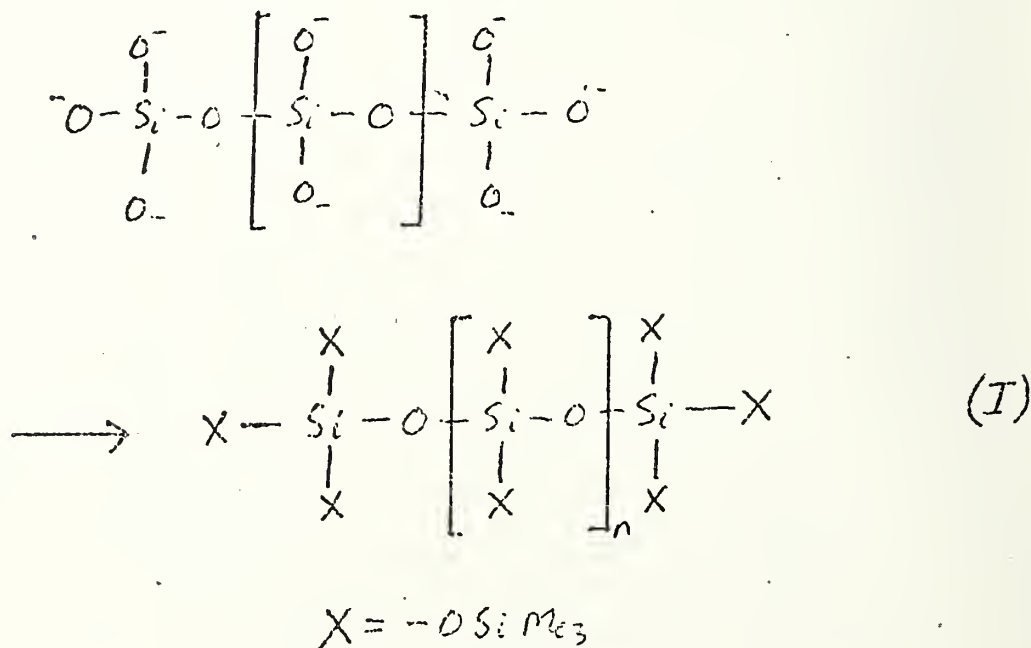
Many mineral silicates may be regarded as inorganic polymers; chains, double chains, sheets and networks are well known (Figure 1).

Trimethylsilylation involves the conversion of  $\equiv\text{Si}-\text{O}-$  sites to  $\equiv\text{Si}-\text{O}-\text{SiMe}_3$ .<sup>3</sup>

The general interest in trimethylsilylation is based on two objectives:

- (a) to provide additional information on silicate structures by the determination of chain lengths and
- (b) to prepare new polyorganosiloxane based materials.

Lentz reported that trimethylsilylation may be achieved using a reaction mixture of concentrated hydrochloric acid, water, isopropyl alcohol and hexamethyldisiloxane. He attempted to apply this reaction to a measurement of silicate chain lengths in sodium silicate solutions<sup>1</sup> and hydrated portland cement pastes<sup>2</sup> by converting the silicate anion to a polyorganosiloxane the molecular weight of which could be measured (I). Masson, with a modified reaction mixture used trimethylsilylation to measure the chain length in lead silicate glasses.<sup>3</sup>



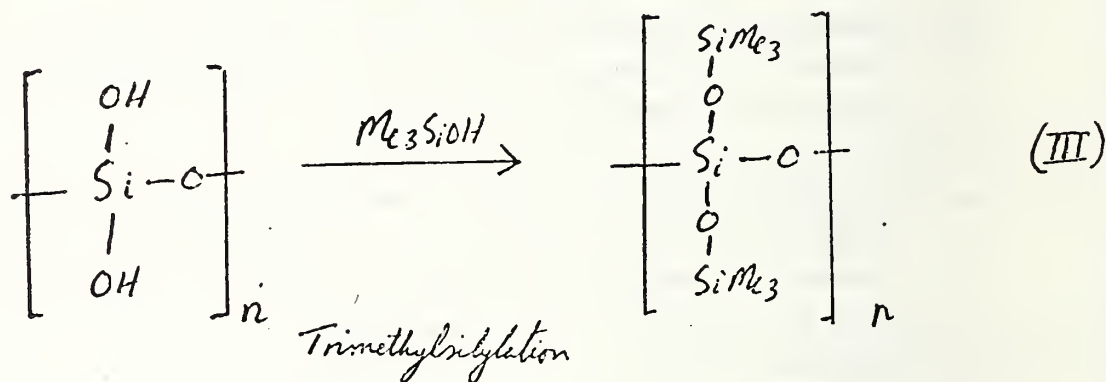
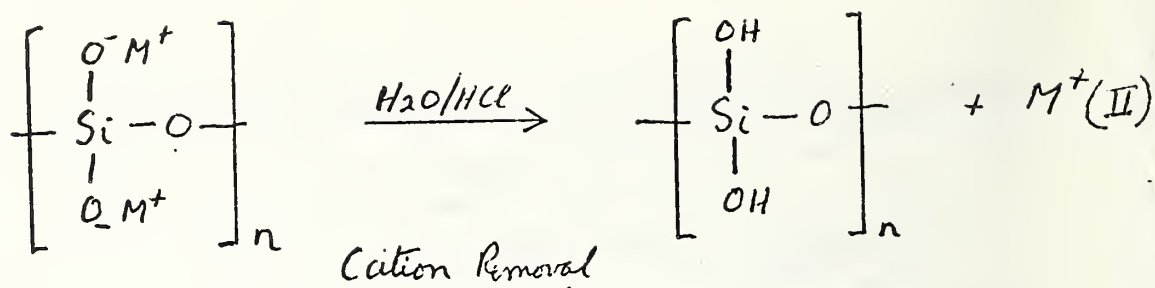
If trimethylsilyl derivatives can be prepared while still retaining the original backbone structure of the silicate there is considerable potential for the preparation of polyorganosiloxanes of both conventional and novel structures, e.g. double chain or ladder polymers, and also sheet polymers. Holliday<sup>4</sup> has discussed the physical properties of the whole polymer spectrum and demonstrated that ~~there~~<sup>there</sup> is a very wide gulf between the properties of, for example, the polyorganosiloxanes and the inorganic silicates. No materials have been prepared which fill this gulf. It is possible that materials of this type may be prepared by partial trimethylsilylation of inorganic silicates.

This paper is a report of a study designed to assess the applicability of the trimethylsilylation technique to a wide range of macromolecular silicates taking examples of chains, double chains and sheets. The silicates which were examined are as follows.

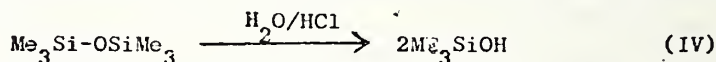
Single chains	Sheets
Diopside	Daphnite
Hedenbergite	Vermiculite
Hypersthene	Prehnite
Bronzite	Apophyllite
Wollanstonite	Biotite
Double chains	Phlogopite
Anthophyllite	Talc
Tremolite	Kaolinite
	Muscovite
	Margarite
	Thuringite

Trimethylsilylation is carried out by heating the mineral (10 g) with a mixture of isopropyl alcohol (50 ml), hydrochloric acid ( $d = 1.18$ , 50 ml) and hexamethyldisiloxane (66.6 ml).

The ideal trimethylsilylation reaction may be represented as shown in (II) and (III) using a single chain silicate as an example. The ideal reaction involves complete removal of cations and the trimethylsilylation of the resulting polysilicic acid with retention of the original silicon-oxygen backbone in the final product.

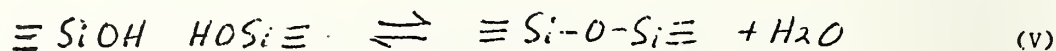


Trimethylsilanol is formed from the hexamethyldisiloxane as shown in (IV).



The minerals examined showed varying degrees of reactivity towards trimethylsilylation at 75° and may be divided into three groups. Group I comprises bronzite, hypersthene, diopside, tremolite, prehnite, talc and kaolinite and shows no reactivity; the mineral is recovered unchanged from the reaction mixture in each case. Group II comprises hedenbergite, wollastonite, anthophyllite, apophyllite and vermiculite in which partial or complete cation removal occurs followed by partial trimethylsilylation to give an insoluble solid. Group III comprises daphnite, biotite, phlogopite, muscovite, margarite and thuringite from which there is complete cation removal to give trimethylsilylated products soluble in organic solvents. Except for biotite, reaction at room temperature gave in each case little or no trimethylsilylation with the recovery of the unreacted mineral.

In Group II minerals, degrees of trimethylsilylation were calculated from C,H analyses. Further evidence for trimethylsilylation rests on infrared spectra and DTA. The infrared spectra of all these products showed evidence for the presence of unreacted Si-OH groups and there is the probability of the development of a silicate type structure formed by the condensation of adjacent Si-OH groups shown in (V).





Calculated degrees of trimethylsilylation are as follows:

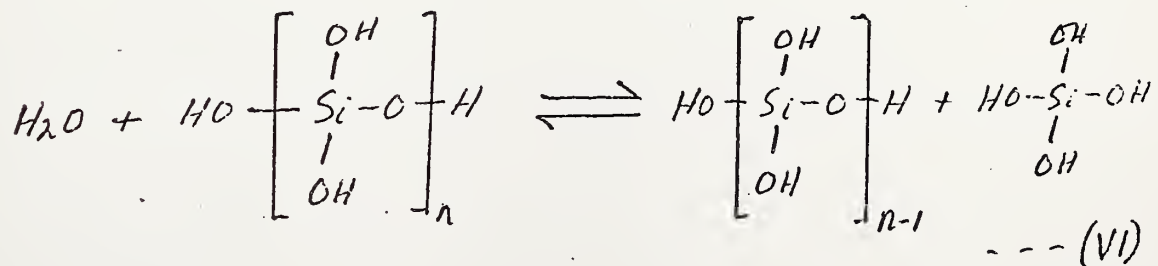
Hedenbergite	14.8%
Wollastonite	14.3%
Vermiculite	89.3%
Apophyllite	16.5%

In the minerals in Group III all the cations were removed. Analytical figures indicate the average representative structures shown in Figure 2.

All these structures receive support from elemental analyses, hydroxyl group determination, molecular weight measurements, infrared,  $^1\text{H}$  n.m.r. and mass spectra.

The success or otherwise of the trimethylsilylation depends in a very complicated way on the structure of the silicate mineral used. The first requirement is that the cations must be leachable by hydrochloric acid. Some general points may be noted with regard to our present work; (a) cation removal is helped by the presence of heavy metal ions, e.g. Fe (cf. hedenbergite, anthophyllite and vermiculite), and (b) the less closely packed is the backbone the more likelihood there is of acid attack (cf. wollastonite and apophyllite). Following cation removal the accessibility of the Si-OH sites to attack by  $\text{Me}_3\text{SiOH}$  will be the controlling factor. Polymerisation/depolymerisation equilibria of the silicic acid will be competing with the trimethylsilylation reaction as shown in (VI).

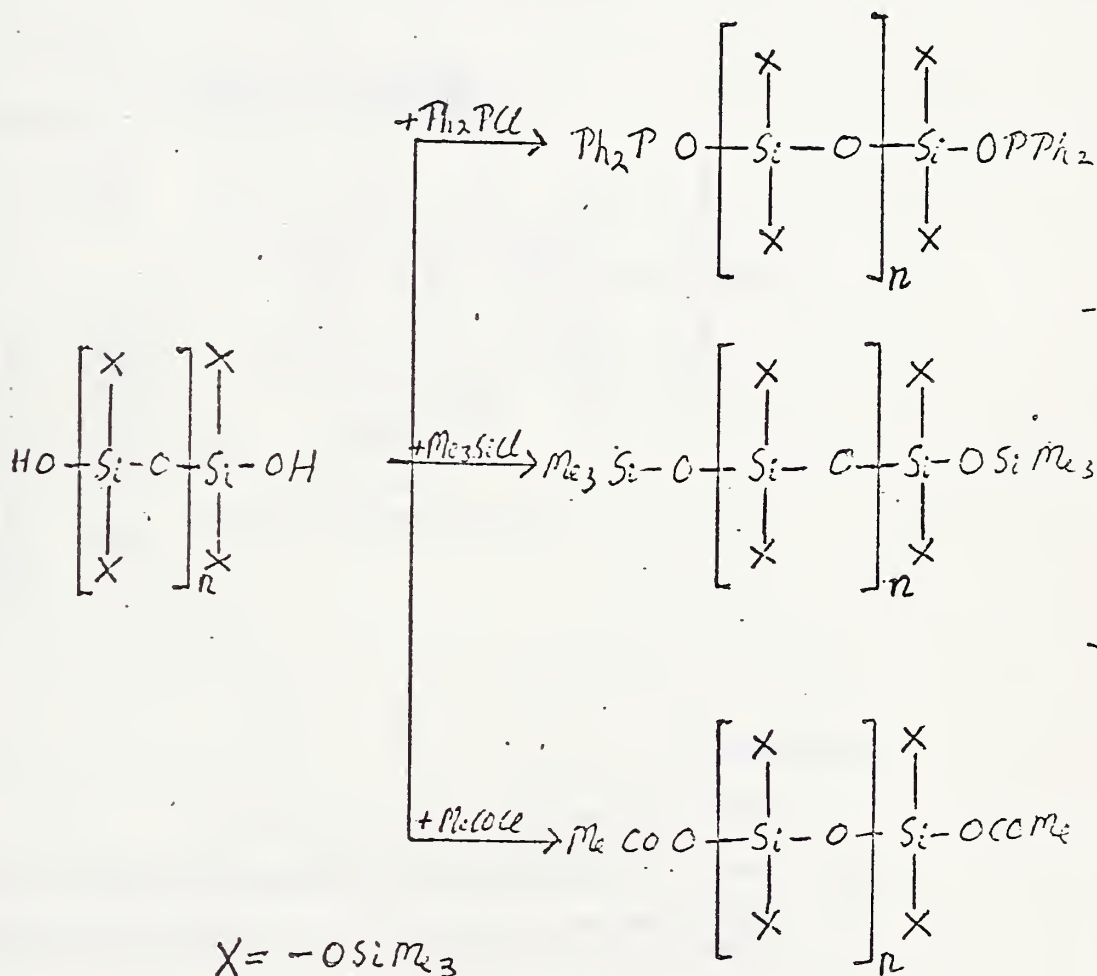
In each case all possible reactions, no doubt, occur to varying degrees, but in the cases of wollastonite and hedenbergite this appears to be important. Apophyllite too falls in this category but here the sheet structure appears to be retained in the product together with some unreacted Si-OH groups and it is possible that this retention of the sheet structure might render the Si-OH sites inaccessible to the incoming group for further reaction.



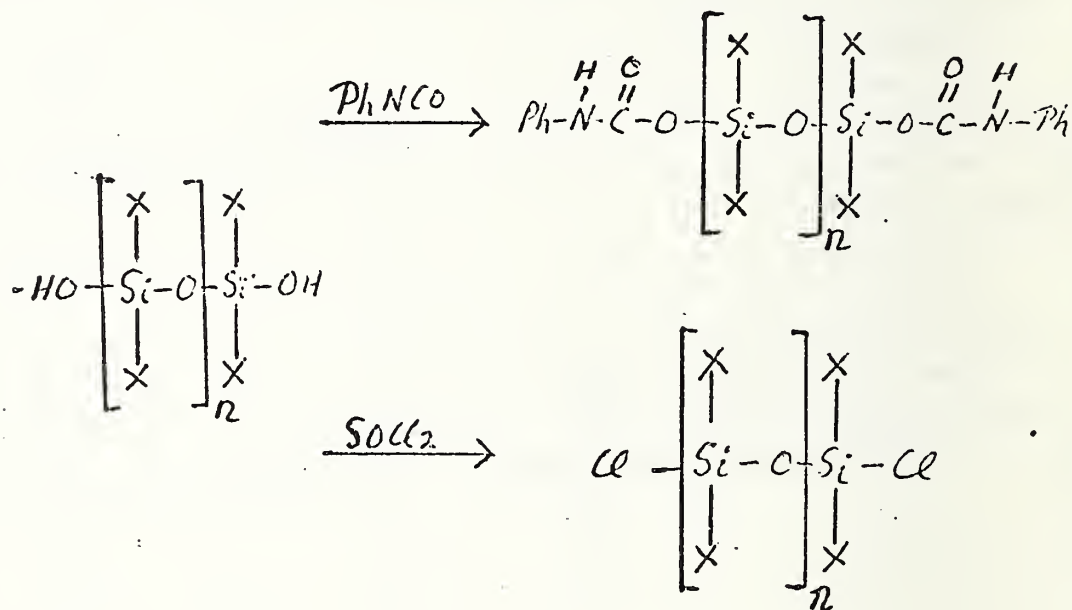
Soluble products appear to be formed when there is a certain degree of replacement of silicon by aluminium in the silicate sheet. Thus with relatively little  $\text{Al}^{3+}$  in the tetrahedral sheet of vermiculite although the cations are removed no soluble products are formed. Biotite, phlogopite and muscovite have approximate Al:Si ratios of 1:3 while margarite and thuringite have approximate Al:Si ratios of 1:1; each of these gave soluble products. Presumably acid attack occurs at the aluminium centre breaking the silicate sheet at these points to form fragments small enough to allow attack by trimethylsilanol and give products of molecular weight small enough to allow solubility in organic solvents. Assuming that fission occurs at the aluminium centres in the silicate sheet, it should be possible to correlate the average molecular weight of the products with the distribution of aluminium in the silicate sheet. Thus margarite and thuringite with high levels of aluminium in the silicate sheet gave low molecular weight products compared with biotite, phlogopite and muscovite which with less aluminium in the silicate sheet gave comparatively high molecular weight products.



The reactivity of the hydroxyl groups has been examined in reactions of biotite and thuringite products with diphenylphosphine chloride, trimethylchlorosilane, acetyl chloride, phenyl isocyanate and thionyl chloride. This work is still in progress but some conclusions have already been reached. Diphenylphosphine chloride, trimethylchlorosilane and acetyl chloride each react to give replacement of the hydroxyl groups e.g.



The reactions involving phenyl isocyanate and thionyl chloride have also been carried out, but as yet the picture is complicated and we are unsure of the type of reaction which has occurred. It is possible that the replacements shown below are accompanied by an appreciable amount of side reaction.



#### References

1. Lentz, C.W. Inorg.Chem. 1964, 3 (4), 574.
2. Lentz, C.W. Spl. Report 90, Highway Research Board, Washington DC 1966, 266.
3. Gotz, J; Masson, C.R.; Jamieson, W.D. Proc Ann. Mtg. Intern.Comm.Glass, Toronto, Sept 3 -6, 1969, 69.
4. Holliday, L. Chemistry.Ind. 1972, 921

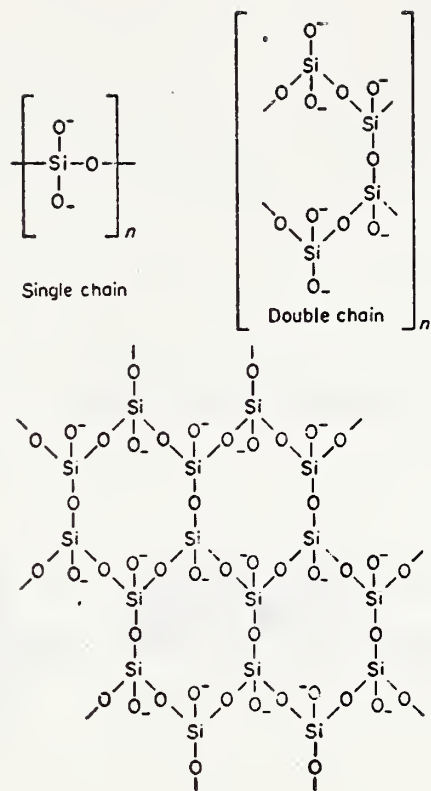
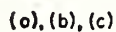


Figure 1. Structure of silicate anions.



(c) from margarite; (f) from daphnite.  $X = \text{SiMe}_3$ .

POLYCARBORANESILOXANES: Part I

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PART I

POLYCARBORANESILOXANES

Extracted from a General Treatise Being Written on Carborane Polymers.





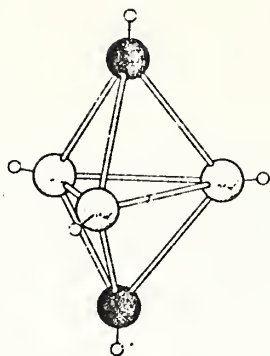
## I. INTRODUCTION

Many copolymers incorporating carborane molecules in the chain, as discussed later, have been synthesized, but the copolymers evoking the most interest, due to their high temperature properties, are the polycarboranesiloxanes. Structurally, the polymers can be visualized simply as polysiloxanes with carborane moieties in the chain. In their physical and chemical properties, general chain structure, and techniques of synthesis, they closely resemble the polysiloxanes. However, because there are electron-deficient carborane molecules in the chain, the polycarboranesiloxanes hold a considerable advantage over the polysiloxanes in high temperature applications. For example, as the stationary phase in gas chromatography, polycarboranesiloxanes can effectively operate with high separation efficiencies at temperatures as high as 400°C. As elastomers, their operational limits lie in the region of 300-350°C. As coatings, where oxidative crosslinking can be utilized, they provide oxidative protection and electrical insulation for the substrate at temperatures in excess of 650°C and, in applications involving stlicate/polycarboranesiloxane composites, at temperatures as high as 1100°C. Silicones cannot compete in these regimes because of their propensity for chain fragmentation and cyclization at temperatures as low as 250-300°C.

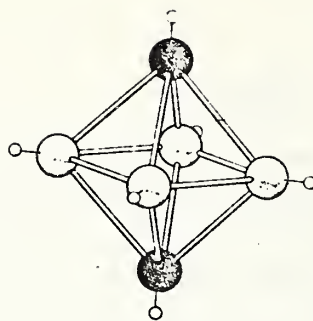
Other carborane copolymers, e.g., polyesters, polycarbonates, vinyl-addition types, etc., have not shown particularly outstanding properties. Consequently, relatively little research activity has been centered on them other than syntheses and minimal characterization studies.

## II. CARBORANES AMENABLE TO POLYMER SYNTHESIS

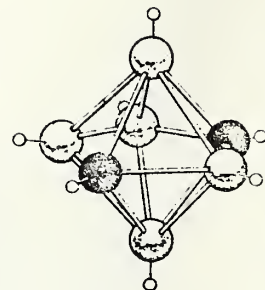
Carboranes are classified as closo-, nido-, and arachno- (Fig. 1-3), corresponding, respectively, to closed-cage, nest, and web structures. Thermal stability and chemical resistance decrease in the order closo- > nido- > arachno because of (and in proportion to the number of) hydrogen bridges on the nido- and arachno-compounds. Consequently,



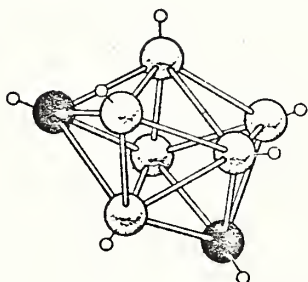
1,5- $C_2B_3H_5$



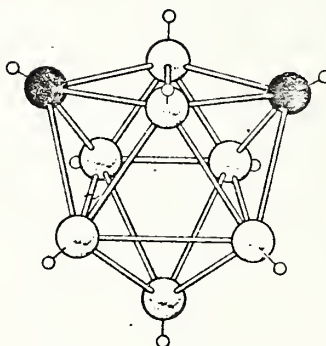
1,6- $C_2B_4H_6$



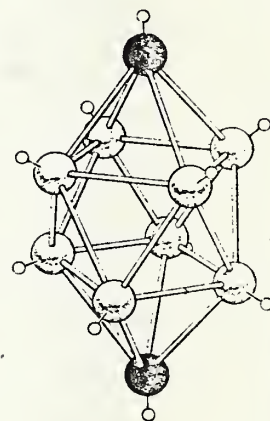
2,4- $C_2B_5H_7$



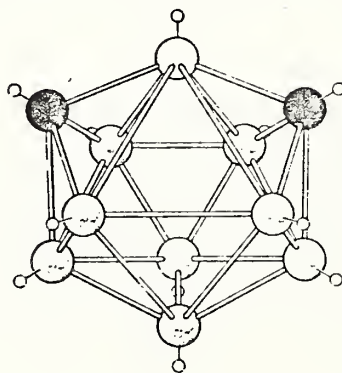
$C_2B_6H_8$



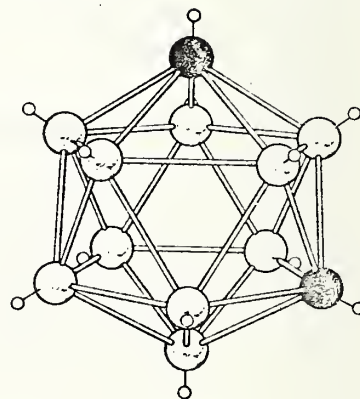
$C_2B_7H_9$



1,10- $C_2B_8H_{10}$

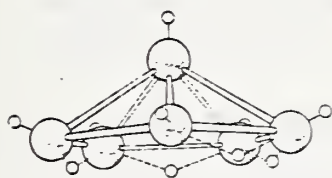


$C_2B_9H_{11}$

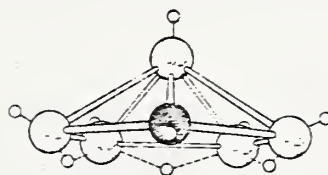


1,7- $C_2B_{10}H_{12}$

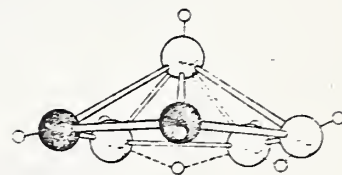
Figure 1. Representative closo-Carborane Structures



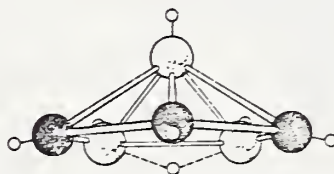
$B_6H_{10}$   
(hexaborane-10)



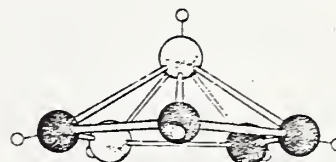
$CB_5H_9$



$C_2B_4H_8$



$C_3B_3H_7$



$C_4B_2H_6$

Figure 2. Representative nido-Carboranes

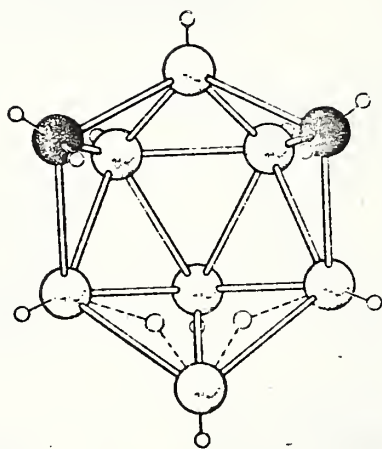


Figure 3. An arachno-Carborane

carborane copolymer systems have to date encompassed only the closo-carboranes (Fig. 1) and primarily  $C_2B_{10}H_{12}$ , and  $C_2B_5H_7$ . The latter two compounds have received the greatest emphasis firstly because of their relatively greater availability and secondly because of the outstanding properties of some of their polymers. However, with the possible exception of the relatively non-stable  $C_2B_3H_5$  compound, the remaining closo-carboranes in Fig. 1 should also be capable of producing polymer systems comparable in many if not all respects to those of  $C_2B_{10}H_{12}$  and  $C_2B_5H_7$ .

### III. CARBORANE STRUCTURAL PARAMETERS

For any polymer system the monomer(s) first of all must have the appropriate functionality to be capable of inclusion in the chain. Closo-carboranes, with two carbon atoms in the molecular cage, possess the requisite difunctionality for linear polymer systems. Short chain, crystalline oligomers have been synthesized by direct carbon carbon bonding between adjacent carborane cages, but the higher molecular weight polymers which have been synthesized to date have all utilized other functional groups attached to the carbon atoms. Examples include dimethylchlorosilyl groups for polycarboranesiloxanes, carboxyl groups for polycarbonates and polyesters, etc., all of which are amenable to polymerization by polycondensation reactions. Similarly, vinyl addition carborane polymers can be prepared from monomers in which a vinyl group is appended to one of the cage carbon atoms.

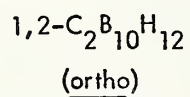
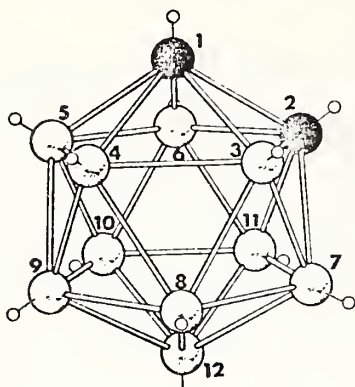
The carbon-attached hydrogen atoms in closo-carboranes possess sufficient acidity to permit substitution reactions to be carried out at these positions. Reactions with Grignard reagents, such as lithium butyl, for example, proceed facily and lead to formation of the dilithiocarboranes, and the lithium atoms in turn can be replaced with an almost unlimited array of other functional groups, including groups amenable to polymerization reactions.

The electron distribution in closo-carborane cages was studied first of all by electrophilic substitution reactions on ortho- and meta- $C_2B_{10}H_{12}$  (Fig. 4), utilizing x-ray diffraction measurements (1) to determine substitution positions.

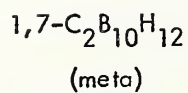
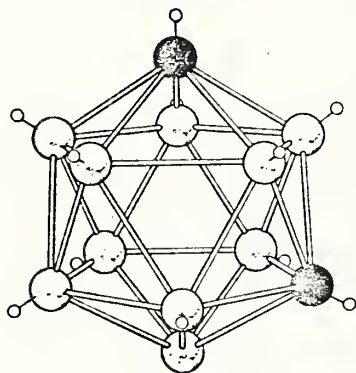
## STRUCTURE

## FORMULA

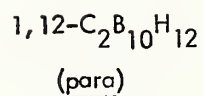
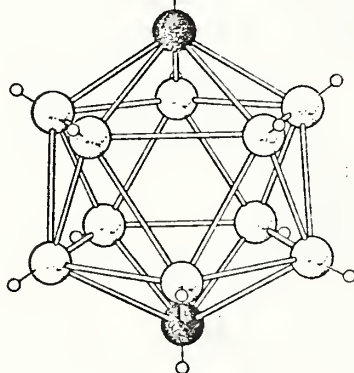
## NAME



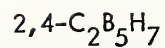
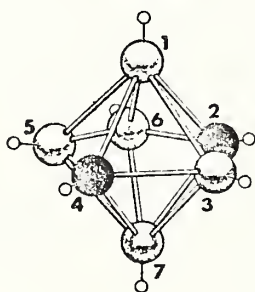
1,2-dicarba-closo-  
dodecaborane-12



1,7-dicarba-closo-  
dodecaborane-12



1,12-dicarba-closo-  
dodecaborane-12



2,4-dicarba-closo-  
heptaborane-7

Figure 4. Nomenclature and Numbering System for Carboranes



Initial substitution was found to occur on the boron atoms opposite the carbon atoms, indicating these to be the positions of highest electron density on the cage. Considerable dipole moment was observed (2), with the carbon constituting the positive pole. On para- $C_2B_{10}H_{12}$ , where the carbons are located directly opposite one another and where all the boron atoms are equivalent, electrophilic substitution occurs randomly. All possible geometric isomers were formed in quantities predicted on a statistical basis.

The electrons in the cage that are not engaged in normal covalent bonding are delocalized throughout the cage and give it a three-dimensional "super-aromatic" character (3), which accounts for the remarkable chemical and thermal stability of these compounds.

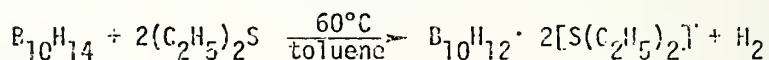
Similarly, analysis by  $^{11}B$ -nmr of the products of Friedel-Crafts alkylation of methyl groups for hydrogen on  $C_2B_5H_7$  indicated preferential disubstitution on the 5,6-borons. Replacement of the terminal hydrogens of  $C_2B_5H_7$  with lithium atoms occurs with equal facility as on the  $C_2B_{10}H_{12}$  compounds, as discussed in the preceding section.

#### SYNTHESIS AND AVAILABILITY OF CLOSO-CARBORANES AND SOME APPLICATIONS

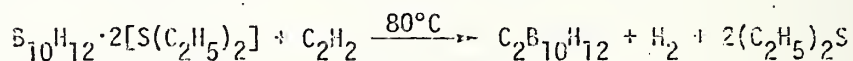
The closo-carborane,  $2,4-C_2B_5H_7$ , is synthesized by direct reaction of acetylene with pentaborane-3 and acetylene, optimized conditions being the 1000 psi flow system in which pentaborane vapor, acetylene, and heat at 500°C react at a second (4). Along with  $2,4-C_2B_5H_7$  are formed  $1,4-C_2B_5H_7$  and  $1,5-C_2B_5H_7$ , along with trace amounts of higher homologs, closo-carboranes ( $C_2B_6H_8$  and  $C_2B_7H_9$ ). Also formed are carborane  $1,2-C_2B_5H_7$  (5) and a variety of carborane  $1,2-C_2B_5H_7$  (6), of which the most important molecular species is  $1,2-C_2B_5H_7$  (7).

distillation on a multi-plate column. Boiling points at 760 mm are 32°C for  $C_2B_5H_7$ , 22°C for 1,6- $C_2B_4H_6$  and -37°C for 1,5- $C_2B_3H_5$ . Complete separation of  $C_2B_5H_7$  from the methylated carborane by-products has not been feasible, but fortunately the methyl groups all appear to be attached to boron atoms and not to the carbon atoms of the carboranes. If even a small concentration of mono-methylated carborane, in which the methyl is attached to a carbon atom, remains in the  $C_2B_5H_7$  fraction, it would serve as a chain terminator in the final polymerization reaction. As little as 0.05 mole percent of this impurity could cut the desired molecular weight drastically. Removal of C-dimethylcarboranes from the  $C_2B_5H_7$ , on the other hand, is not important since these are non-functional and cannot interfere with polymerization.

Preparation of the icosahedral  $C_2B_{10}H_{12}$  carboranes until recently has been carried out by solution phase reaction of decaborane-14 with acetylene. The first step in the synthesis involves preparation of a diligand of decaborane, a typical synthesis being the reaction of decaborane-14 with diethylsulfide (7).



The next step involves addition of the acetylene, which is bubbled through the solution over an extended period of time.



In addition to the reaction of acetylene with the diligand to give  $C_2B_{10}H_{12}$  carboranes, it is possible to use almost any acetylenic compound in this reaction and thereby obtain modified carboranes with pendant groups on one or both cage carbon atoms. A specific example for polymer chemistry is the reaction of vinylacetylene with the diligand, giving a 1-vinylcarborane (Fig. 5). Vinyl addition polymers using this monomer have been prepared, as discussed later.

Based on decaborane-14 as starting material, the yields of carborane produced by the diligand solution chemistry technique run about 80%. This figure, however, can be somewhat misleading, in that the yield is



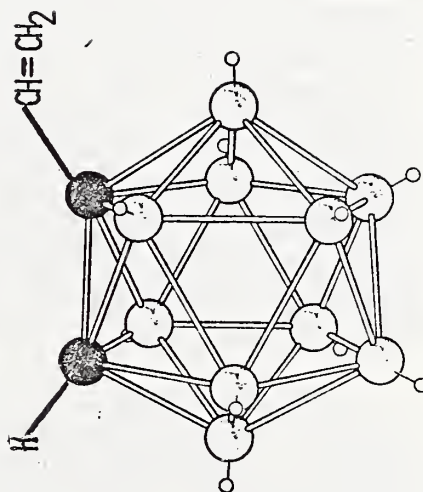


Figure 5. Preparation of the vinyl-pendant carborane.

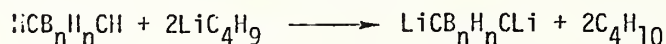
based on sodium tetrahydroborate,  $\text{NaBH}_4$ , which is a precursor (via di-borane) for the preparation of decaborane-14, then the yields of carborane are more on the order of 20-30%. Consequently,  $\text{C}_2\text{B}_{10}\text{H}_{12}$  carboranes produced by this method are very expensive commodities. The same situation is true for the smaller carboranes based on pentaborane-9, though not as severe because yields of pentaborane-9 from  $\text{BH}_4^-$  are about threefold better than for decaborane-14 from  $\text{BH}_4^-$ .

Recently, however, a greatly improved method for producing  $\text{C}_2\text{B}_{10}\text{H}_{12}$  directly from  $\text{BH}_4^-$  and acetylene has been developed by Union Carbide Corporation, although details of the syntheses have not been revealed. Presumably, it is based on a technique first investigated by Callery Company (8) wherein  $\text{BH}_4^-$  is transformed into a higher molecular weight ion or neutral molecule, such as  $\text{B}_{10}\text{H}_{10}^{2-}$ ,  $\text{B}_{10}\text{H}_{13}^-$  or  $\text{B}_{10}\text{H}_{13}$ ·ligand. If the intermediate is ionic, then neutralization with an acid would be required to form the corresponding neutral borane before treatment with acetylene to produce the  $\text{C}_2\text{B}_{10}\text{H}_{12}$  carborane. The overall process, in any event, represents a significant advance in lowering the cost of carboranes and making them available in the near future in reasonably large quantities. Even a yield of 40-50% would be a big improvement over the old method because of the simplicity of the process.

The three  $\text{C}_2\text{B}_{10}\text{H}_{12}$  carborane isomers are all solids at room temperature. Melting points are 295°, 270°, and 260°C, respectively, for the ortho, meta and para configurations. The ortho compound converts quantitatively into meta by thermal rearrangement above 450°C, but conversion into the para compound requires significantly higher temperatures and is a low yield reaction accompanied by fragmentation and cage fusion. Purification of the parent carboranes can be accomplished by recrystallization from ether or acetone.

## V. DILITHIOCARBORANES — MONOMER PRECURSORS

The dilithio derivative of a closo-carborane is prepared by reacting the parent carborane with a lithium alkyl, usually the butyl derivative, in an ether/hydrocarbon solvent.

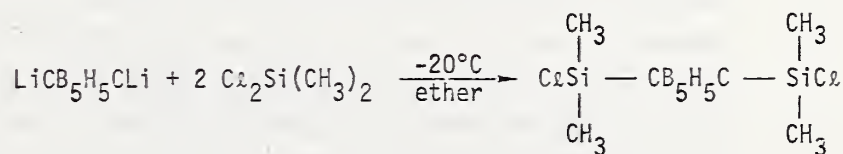


The dilithio derivative of  $C_2B_5H_7$  is generally synthesized at  $-30^\circ C$ , while that of  $C_2B_{10}H_{12}$  requires  $0^\circ C$ .

The carborane is dissolved in a 60/40 diethylether/hexane solution, and then, in an inert atmosphere and with vigorous stirring and supplementary cooling, a 15 weight percent solution of lithium butyl in hexane is added at a rate sufficiently slow to preclude any increase in temperature above the initial level. Approximately 10% excess lithium butyl above the calculated stoichiometric amount is added to insure near-quantitative conversion of the carborane into the dilithio salt. The mono-lithium salt forms almost immediately, but substitution of the second lithium atom requires extended time and somewhat higher temperature. Generally, after all of the lithium butyl has been added, the reaction is allowed to digest overnight at room temperature.

The mono-lithium salt is soluble in the ether/hexane solvent, but the dilithio salt forms a yellowish gummy ether complex, which must be kept suspended by vigorous stirring. With the  $C_2B_5H_7$  carborane, the dilithio salt/ether complex is spontaneously flammable in air, but removal of the last vestiges of ether permits handling in air. The  $C_2B_{10}H_{12}$  derivative, on the other hand, is not spontaneously flammable even as the ether complex.

The dilithio salt can be concentrated by removing all or part of the ether/hexane solvent by vacuum evaporation, or it can be left in the solvent mixture for the next step, i.e., formation of the monomer. Bis-silyl monomers, for example, are formed by reacting the dilithio salt of the carborane with dimethyldichlorosilane, as follows:



( $C_2B_5$ -monomer)

## VI. IMPORTANT PARAMETERS FOR CARBORANE POLYMER SYNTHESSES

The vast majority of carborane-containing polymers are synthesized by polycondensation reactions, i.e., by splitting out a molecule, usually water, from the propagating chain. For condensation-type polymerizations, three very important factors must be considered for the achievement of high molecular weights. These are:

- High monomer purity, i.e., extremely low concentrations of chain-terminating species;
- Precise stoichiometry between reacting co-monomers when copolymers are synthesized;
- High conversion rates for polymerization.

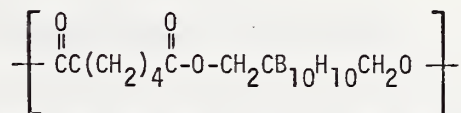
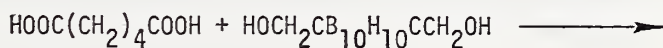
Consider first the problem of purity and, for purposes of illustration, assume a polycondensation reaction involving dimethylsilane diol, which forms when dimethyldichlorosilane is hydrolyzed. If the reaction mixture contains 90 mole percent of the desired monomer,  $(\text{CH}_3)_2\text{SiCl}_2$ , and 10 mole percent of the chain-termination species,  $(\text{CH}_3)_3\text{SiCl}$ , then, on a statistical average, nine molecules of the dimethylmonomer will join together until terminated at one end by a molecule of the trimethyl compound. An additional nine dimethylmonomers will then propagate on the live end of the above chain until it too is terminated by a second trimethyl compound. The number of repeating units in this chain, excluding the terminating species, will be  $9 \times 2 = 18$  and the molecular weight will be  $18 \times 74 = 1332$ . Similarly, if there is only one mole percent of chain-terminating species, the number of repeating units will be  $99 \times 2 = 198$ , and the molecular weight will be  $198 \times 74 = 14,652$ . The table below shows the relationship between molecular weight and various concentrations of chain-terminating molecules for polydimethylsiloxane synthesis.

Table 1. Effect of chain-terminating impurity in the preparation of polydimethylsiloxane

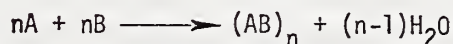
Monomer Concentration	Chain-Terminating Species	Average No. of Repeating Units	Average Molecular Weight
90 mol %	10 mol %	18	1,332
99	1	198	14,652
99.9	0.1	1,998	148,000
99.95	0.05	3,998	296,000
99.975	0.025	7,998	592,000
99.990	0.010	19,998	1,500,000

A desirable molecular weight for this polymer for many applications is about 600,000, which represents 8,000 repeating units. If as little as 0.05 mole percent of trimethylmonomer is initially present, the molecular weight will be only half of the desired value; if 0.1 mole percent is present, the molecular weight will be one-fourth as much as desired. Molecular weight differences of these magnitudes can mean significant differences in the polymer's physical properties, e.g., large differences in viscosity if it is an oil and differences in strength if it is to be an elastomer.

Consider next the problem of stoichiometry in the polymerization of two co-monomers and assume that the final product is a polyester made by copolymerizing adipic acid,  $\text{HOOC}(\text{CH}_2)_4\text{COOH}$ , with a carborane diol, such as bis-hydroxymethyldodecaborane:



Schematically, this can be represented as





In this case the molecular weight of A is 146, while that of B is 204; molecular weights of the participating units in the polymer chain are  $146-18 = 128$  for A and  $204-18 = 186$  for B.

If the reacting mixture contains only half as many moles of A as B, then the polymer chains will, on the average, grow to only three units long, i.e., BAB, before terminating. If the reaction mixture contains 40 mole percent of A and 60 mole percent of B (2:3 ratio), then the polymer chains will grow to five units, i.e., BABAB. Table 2 shows the influence of the relative monomer concentrations on chain length and molecular weight — assuming 100% conversion into polymer, a feat which experimentally can be approached but never achieved (9).

Table 2. The influence of monomer stoichiometries on chain length and molecular weight of the carborane polyester,  $\{\text{COC}(\text{CH}_2)_4\text{COO}-\text{CH}_2\text{CH}_{10}\text{H}_{10}\text{CCH}_2\text{O}\}_n$  represented as  $(\text{AB})_n$ , and assuming 100% conversion.

<u>mole % A</u>	<u>mole % B</u>	<u>chain units</u>	<u>molecular weight</u>
33	67	3	500
40	60	5	814
49	51	50	7,850
49.5	50.5	100	15,700
49.9	50.1	500	78,500
49.95	50.05	1,000	157,000
49.99	50.01	5,000	785,000
49.995	50.005	10,000	1,570,000

The chain length in the previous table is calculated simply by the expression:

$$\text{No. of units} = \frac{1}{\text{Mole fraction B} - \text{Mole fraction A}}$$

The percent conversion of monomer into polymer is also a very important factor in determining the final chain length in polycondensation reactions (9). In table 2, for example, if the conversion were 99% rather than 100%, then for the polymer consisting of 100 units, one out of 100 links would not have been formed, and the molecular weight would

be only half of that shown, or 7,850. For the polymer consisting of 1,000 units, ten links would not have formed, and the molecular weight would be only one-eleventh of that shown, or 14,300 rather than 157,000, a dramatic difference.

Similarly, for 99.5% conversion, for 1,000 chain units five would not have formed, and the molecular weight would be  $157,000 \div 6 = 26,000$ . Table 3 shows data from table 2 recalculated on the basis of 99.9%, 99.5% and 99% conversion.

Table 3. The effect of percent conversion on chain length and molecular weight of the polyester shown in Table 2.

Conversion:	No. of Units per Chain				Molecular Weight			
	100%	99.9%	99.5%	99%	100%	99.9%	99.5%	99%
	100	91	67	50	15,700	14,270	10,470	7,850
	500	333	143	83	78,500	52,300	22,430	13,080
	1,000	500	167	91	157,000	78,500	26,170	14,270
	5,000	833	192	98	785,000	130,800	30,190	13,390
	10,000	909	196	99	1,570,000	142,700	30,780	15,540

One of the primary reasons why completely quantitative conversions in polycondensation reactions are not realized is the fact that they are equilibrium reactions. (10) where one mole of water is formed for each condensation. Hence, the water must be removed from the equilibrium to increase the conversion and thereby achieve high molecular weights. However, even with high molecular weights a small amount of water still belongs to the equilibrium, and the amount of water remaining is a function of the equilibrium constant (10).

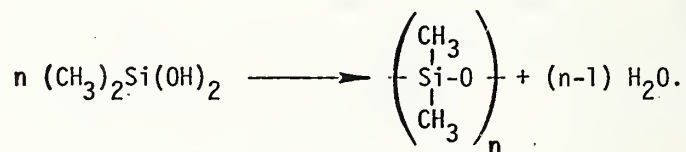
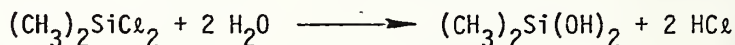
In summary, the purity, the stoichiometry, and the degree of conversion are very important factors in polycondensation reactions, and this covers the large majority of polycarborane syntheses. The achievement of high molecular weights has been a difficult problem until very recently, particularly with polycarboranesiloxanes, and the reasons cited here, particularly purity, have been responsible for this problem. Up

until as recently as 1973, polycarboranesiloxane molecular weights above 20,000 were rarely achieved, and the desired strength and toughness of the elastomers were consequently lacking.

## VII. POLYCARBORANESILOXANE SYNTHESSES

Silicone Analogies. The methods of synthesis of silicone polymers, or polysiloxanes, are closely allied with the methods of synthesis of polycarboranesiloxanes, and in fact the latter can be regarded as modified silicones. The carborane and silane monomers possess the same types of functionalities, and hence their polymerization mechanisms are similar.

A typical silicone polymerization is that of dimethyldichlorosilane, which is reacted with water to form the silanol. The silanol then undergoes polymerization by condensation, splitting out one molecule of water for each condensation. The overall reaction is as follows:



With the simple addition of water to the monomer, generally in the presence of an ether solvent such as dioxane,  $n$  can vary from that of low molecular weight trimers, tetramers, etc., up to fairly large values that correspond to straight chain (linear) polymers. The addition of catalysts, buffers, different solvents, etc. can change the distribution of molecular weights over a large range. However, high molecular weight silicones are best achieved by synthesizing low molecular weight cyclic oligomers, generally trimers and tetramers, and subjecting these oligomers to rigid purification procedures. The oligomers, in the



presence of catalysts, then can be polymerized to very high molecular weight linear polymers (11). In this way the problems of purity, stoichiometry and high conversion that are inherent in polycondensation reactions are overcome.

Cyclic polysiloxane trimer, tetramer, etc. are formed in appreciable quantities in the polycondensation of hydrolyzed dichloromonomer, and these are recovered (after HCl evolution and solvent evaporation) by distillation of the product mixture. At 760 mm the boiling points are 134°C for the trimer and 175°C for the tetramer; cyclic compounds with higher values of  $n$  are recovered by distillation at reduced pressures (12). Cyclic polysiloxanes can also be obtained by heating linear polysiloxanes to 350-400°C and removing the volatile fragmentation products from the still pot with a stream of nitrogen. Trimer and tetramer are then subsequently recovered from this distillate by another fractional distillation, as above.

High molecular weights can be obtained from the cyclic oligomers by either acid or base catalysis. In acid catalysis the oxygen atom in the polymerizing chain is an electron donor for the proton of the acid, while in base catalysis the base is a donor for the silicon atom, thereby allowing the silicon to take on additional valency ( ). Both phenomena are ionic in character but opposite in their polarizing characteristics, i.e.,



Base catalysis of the cyclic tetramer, for example, is achieved with absolutely dry KOH (14), and the mechanism involves OH<sup>-</sup> attack on a silicon atom and K<sup>+</sup> attack on an adjacent oxygen. The ring opens into a chain with K<sup>+</sup> and OH<sup>-</sup> ends. These then catalyze further ring openings and polymerizations, and the net result is formation of high molecular weight polymers. Water is excluded from this system.

Similarly, a catalytic amount of concentrated  $\text{H}_2\text{SO}_4$  can induce the formation of high molecular weight polymers from these same oligomers, again in the complete absence of water ( ).

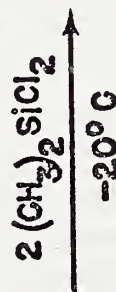
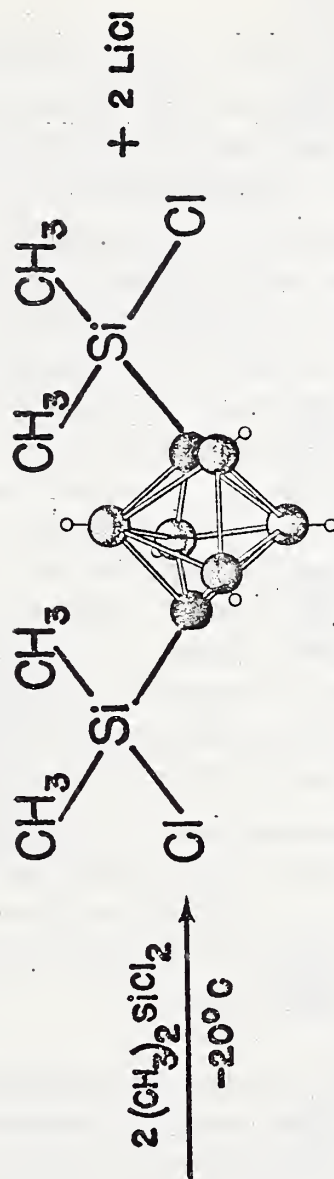
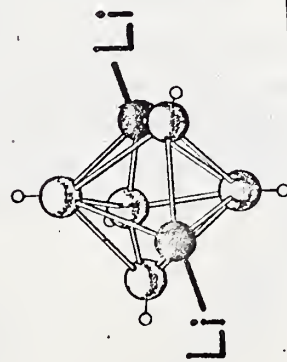
The point of this discussion is to emphasize the techniques for achieving high molecular weights with silicones, utilizing the cyclic oligomers to attain the requisite high purities and high conversions. Carborane-siloxane polymers, on the other hand, do not generally cyclize and hence cannot take advantage of this mode of purification. These factors are important but have not generally been emphasized in previous polycarborane literature.

Finally, it should be mentioned that high molecular weights are not necessarily always desired, and lower molecular weight polymers, for example oils of certain specific viscosities, are sometimes required. These materials, however, are also readily obtainable by the above same techniques but with the deliberate addition of controlled amounts of end-capping monomers, such as trimethylchlorosilane, to limit chain lengths. In this same context, it is frequently desired to impart elastomeric properties to a polymeric resin, and for this purpose tri- and tetrafunctional monomers can be added to the reacting mixture to impart specific amounts of crosslinking into the resin.

bis-Silyl Carborane Monomers. The dilithio salts (Section V) are suitable precursors for just about any category of condensation-type monomers, including the bis-silylated carboranes from which polycarborane-siloxanes are made.

The preparation of the  $\text{C}_2\text{B}_5$ -monomer from the dilithio salt is illustrated in Fig. 6. The ether/hexane slurry of the dilithio salt is allowed to flow very slowly into an ether solution of dimethyldichlorosilane, maintained at  $-20^\circ\text{C}$ . An excess of the silane compound is maintained to insure complete silylation.

When the reaction is finished, the ether, hexane, and unreacted silane are stripped off at reduced pressures, and finally the monomer is removed by vacuum distillation (B.P.  $65^\circ\text{C}$  at one torr). The main



2,4-bis(chlorodimethylsilyl)-2,4-dicarba-closo-heptaborane-7

# **[C<sub>2</sub>B<sub>5</sub> MONOMER]**

Figure 6. The preparation of the C<sub>2</sub>B<sub>5</sub> Monomer

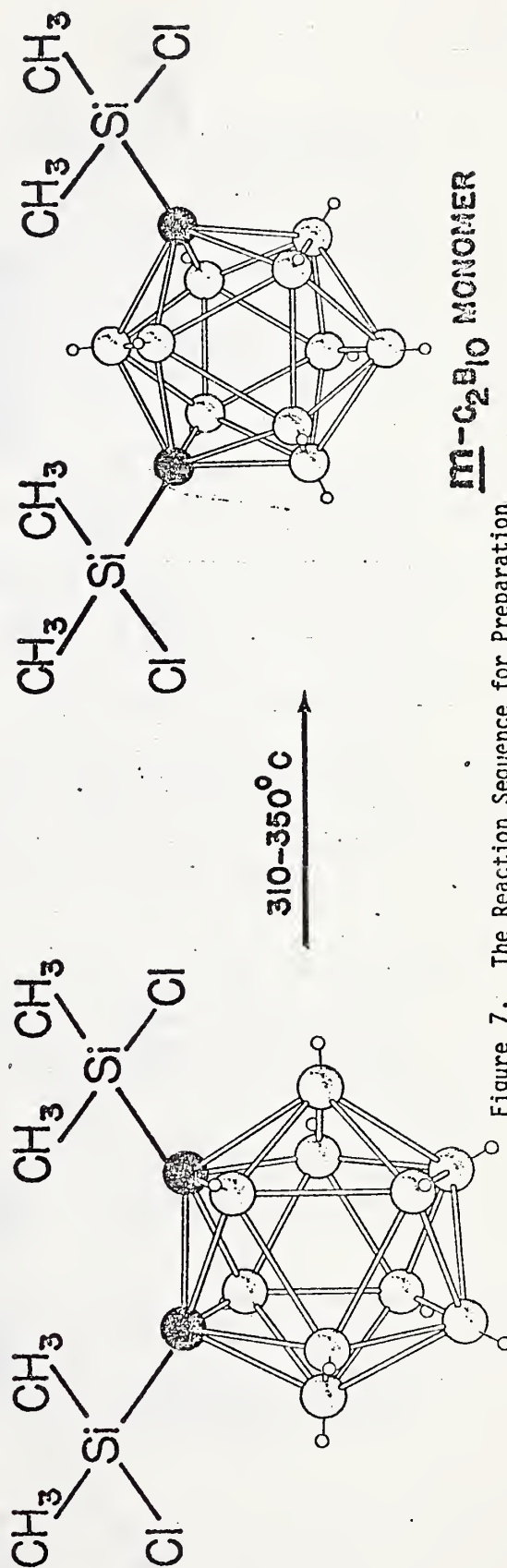
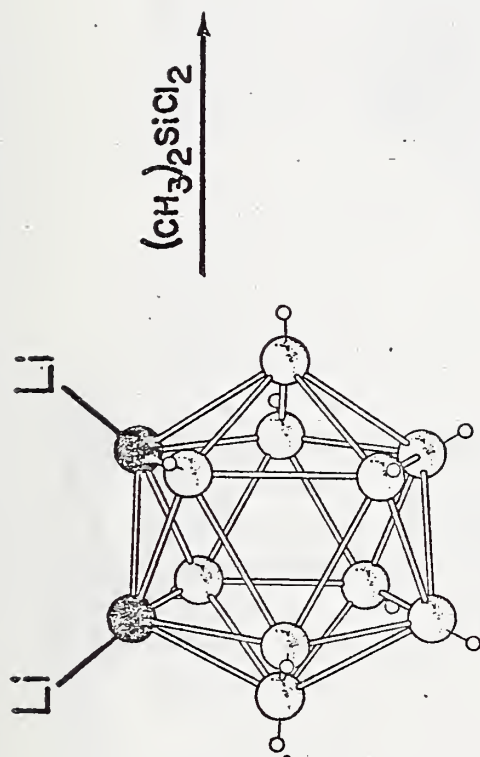
impurity (B.P. 46°C at 1 torr) is the monochloromonomer, wherein the second chlorine atom has been replaced by a hydrogen atom. This impurity can be transformed into the dichloromonomer by distilling it in the presence of aluminum chloride and acetyl chloride.

The preparation of  $C_2B_{10}$ -monomers involves the same general chemistry as that of the  $C_2B_5$ -monomer except that with  $C_2B_{10}$  there are three potential monomers, depending on whether  $C_2B_{10}H_{12}$  is to have ortho, meta or para configuration (Fig. 4).  $m-C_2B_{10}H_{12}$  is quantitatively derivable from  $o-C_2B_{10}H_{12}$  by thermal rearrangement above 450°C, but it has been found to be more convenient to prepare first the bischlorodimethylsilyl derivative of  $o-C_2B_{10}H_{12}$ , which is the ortho- $C_2B_{10}$  monomer, then convert it to the m-configuration because this rearrangement takes place at much lower temperatures ( $\sim 300^\circ C$ ) than that of the parent carborane (15). The sequence is shown in Fig. 7. Conversion of the  $m-C_2B_{10}$ -monomer into  $p-C_2B_{10}H_{12}$ -monomer, however, is not feasible because the requisite temperatures destroy the monomer. In this case it is necessary to prepare first the  $p-C_2B_{10}H_{12}$  parent compound, then synthesize its monomer by normal lithiation and silylation procedures.

The experimental details of synthesis of the bis-silyl monomers of the three isomers of  $C_2B_{10}H_{12}$  have been extensively reported in the literature (16). The silylation reaction is carried out at 0°C, and the monomers can be purified by vacuum fractionation but are usually purified by recrystallization from ether.

#### Carborane-Siloxane Polymerization by Ferric Chloride Catalyses.

One of the earliest attempts to synthesize polycarboranesiloxanes involved condensation polymerization of the bis-(chlorodimethylsilyl)-monomer of ortho- $C_2B_{10}H_{12}$  (17). However, chain polymerization was unsuccessful due to the tendency of the condensation product to form a five-membered exocycle (Fig. 8) in almost quantitative yields. This compound was observed to possess extreme thermal stability, surviving 500°C with comparative ease. The same phenomenon occurred when the monomer was reacted with ammonia except that the product here was a very stable cyclic imide. Electron resonance in this ring, enhanced tremendously by the electron deficient



**m-C<sub>2</sub>B<sub>10</sub> MONOMER**

Figure 7. The Reaction Sequence for Preparation of the ortho- and meta-C<sub>2</sub>B<sub>10</sub> Monomer



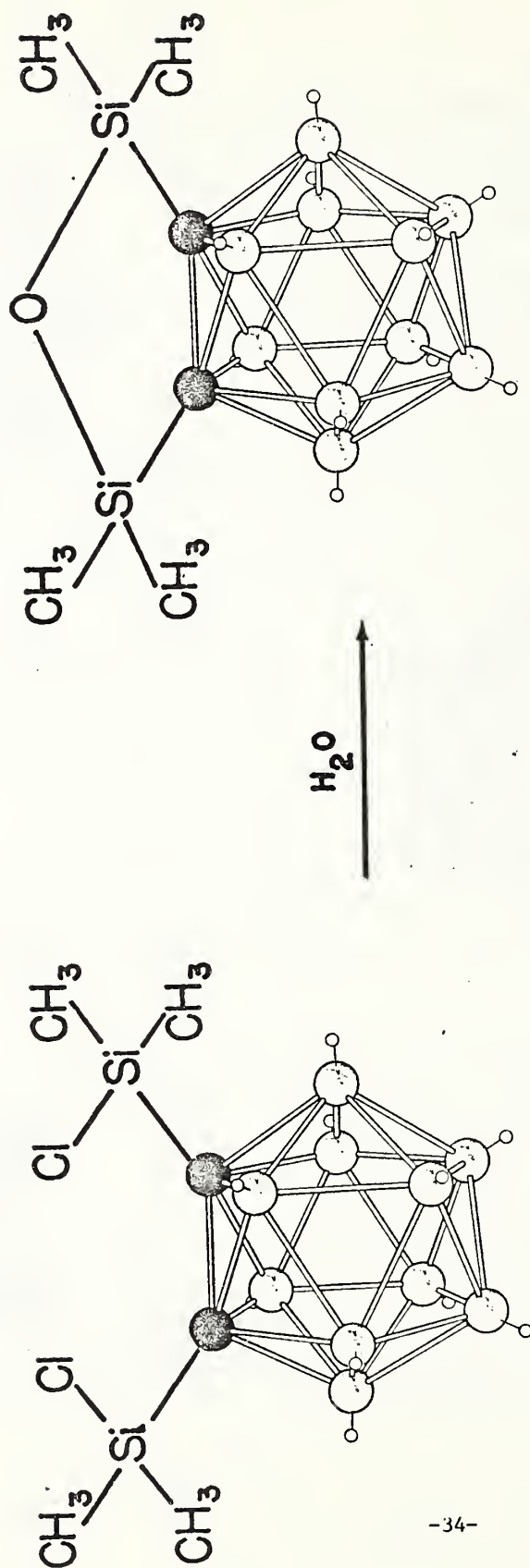


Figure 8, Formation of the Five-Membered Exocycle on Hydrolysis of the ortho-C<sub>2</sub>B<sub>10</sub> Monomer

cage in conjunction with the siloxy moieties, gives it extraordinary stability.

The exocyclic ring compound can be obtained in very high purity, but whether the ring could be catalytically induced to open up and form the linear high molecular weight polymer is problematical. If so, it would be an ideal way to generate both the ortho and meta forms of this homo-polymer, since the ortho form can be converted quantitatively to meta by heating above about 300°C.

When the ortho monomer was found to form the exocycle, research efforts were switched to the meta monomer which does not cyclize because the carbon atoms in the cage are nonadjacent. The first attempts to polymerize the meta carborane monomer involved hydrolysis of the bis(chloro-dimethylsilyl) derivative by the simple addition of water to an acetone solution of the monomer at room temperature (18). The diol formed readily, but it could not be induced to undergo polycondensation. Subsequently, techniques that had worked in silicone chemistry (19), i.e., a ferric chloride catalyzed polymerization reaction between dichloromonomer and dimethoxymonomer (made from the dichloro-compound by methanolysis) were tried and found to work (20). The reaction was carried out neat (no solvents) at temperatures ranging up to 190°C. Methyl chloride is a product of the reaction.

Similarly copolymerization of the dimethoxy carborane monomer with suitable proportions of dichlorodimethylsilane opened the way to synthesis of the entire family of "SiB polymers," which later were designated as Dexsil polymers for commercial sale. Experimentally, the liquid co-monomers were placed in a flask along with about 2 mole percent  $\text{FeCl}_3$ , then heated under vacuum with continued stirring for a period of about four hours. Purification of the resin was carried out by recrystallization from hot xylene.

The "SiB" designation is a convenient method of identifying the polycarboranesiloxanes. For example, 10-SiB-1 indicates that the polymer is based on the bis-silylated  $\text{C}_2\text{B}_{10}\text{H}_{12}$  carborane and has one oxygen atom per repeating unit. 5-SiB-2 indicates the  $\text{C}_2\text{B}_5\text{H}_7$  carborane, with two

oxygens per repeating unit; it is made by co-condensation of the  $C_2B_5$ -monomer with dimethyldichlorosilane.

A number of years after the successful synthesis of the 10-SiB polymers, when the smaller closo-carborane,  $C_{10}B_{10}H_{12}$ , became available in sufficient quantities, this same ferric chloride catalyzed polymerization reaction was applied to  $C_2B_5$ -based carborane monomers (21). The technique was again successful, producing 5-SiB-1, a hard wax, as the first Pentasil polymer. One important difference was immediately noted in that the Pentasil polymer was more tractable and lower melting than the corresponding Dexsil polymer. Whereas  $T_m$  was 260°C for 10-SiB-1, it was found to be only 70°C for 5-SiB-1. The transition temperatures for the 5-SiB-1 were roughly comparable to those for 10-SiB-3.

This observation then spurred efforts to try to develop a 5-SiB-1 elastomer, or at least an elastomeric polymer requiring substantially fewer siloxy groups in the chain than did the Dexsil polymers. With this end in mind, the idea of disrupting the chain symmetry of the 5-SiB-1 polymer by randomly inserting large  $C_{10}B_{10}$ -moieties in the chain was originated. Hopefully, such a modified SiB-1 polymer would either be elastomeric or could be made elastomeric under ambient conditions. When this modified 5-SiB-1 polymer was synthesized, again by ferric chloride catalyzed reaction between the methoxy- and chloromonomers, it was indeed found to be an elastomeric resin. Its physical and chemical properties were approximately the same as those of elastomeric 10-SiB-3 (Dexsil 300).

Unfortunately, in the case of both the Pentasil and Dexsil polymers at that time, the high temperature synthesis and/or post-treatment introduced crosslinks into the polymer. The crosslinking probably is caused by a Friedel-Craft type attack on the cage, wherein the ferric chloride induces methyl group bridging between adjacent chains.

Except for the unmodified 5-SiB-1 and 10-SiB-1, every polymer synthesized by ferric chloride catalysis was either elastomeric or intractable because of excessive crosslinking, and no two samples ever appeared to have the same consistency. Fortunately, other techniques soon



were discovered (about 1970) which made available for the first time long chain linear polymers. One technique was room temperature alcoholysis, suitable for synthesis of Pentasil polymers (22); another was a low temperature (0°C) hydrolysis, devised for synthesis of certain Dexasil polymers (23); a third was an acid-catalyzed condensation of  $C_2B_{10}$ -monomers (23). More recently a fourth approach, involving silanes with facile leaving groups, has been successfully applied to the synthesis of very high molecular weight 10-SiB-2 polymers (24).

Synthesis of Pentasil Polymers by Alcoholysis. In carrying out a ferric chloride catalyzed polymerization, one of the preliminary steps involves preparation of the dimethoxymonomer by reacting the dichloromonomer with methanol. In the course of one such methanolysis reaction with  $C_2B_5$ -dichloromonomer, it was noticed that a white precipitate had formed after standing for several days (22). Infrared analysis then showed this precipitate to be a Pentasil polymer with some additional B-O bonding attributable to B-OR groups on the carborane cage. The methoxy monomer had undergone a polycondensation reaction and formed a 5-SiB-1 polymer, but, unfortunately, the methanol had also attacked the carborane cage. A systematic search then indicated that a tertiary alcohol, such as t-amyl, was a suitable reagent for any and all 5-SiB (random) polymers. Molecular weights up to 5,000 were obtained with this method. Copolymers made with more than about 20 mole percent dimethyldichlorosilane were found to be oily liquids, while the addition of tri- or tetra-functional monomers made them elastomeric gums, a typical formulation being:

$C_2B_5$ Monomer	67 mole %
$(CH_3)_2SiCl_2$	25 mole %
$CH_3SiCl_3$	8 mole %

Polycarboranesiloxanes by Hydrolytic Polycondensation. The  $C_2B_{10}$  monomer, in contrast to the  $C_2B_5$  monomer, is not amenable to formation

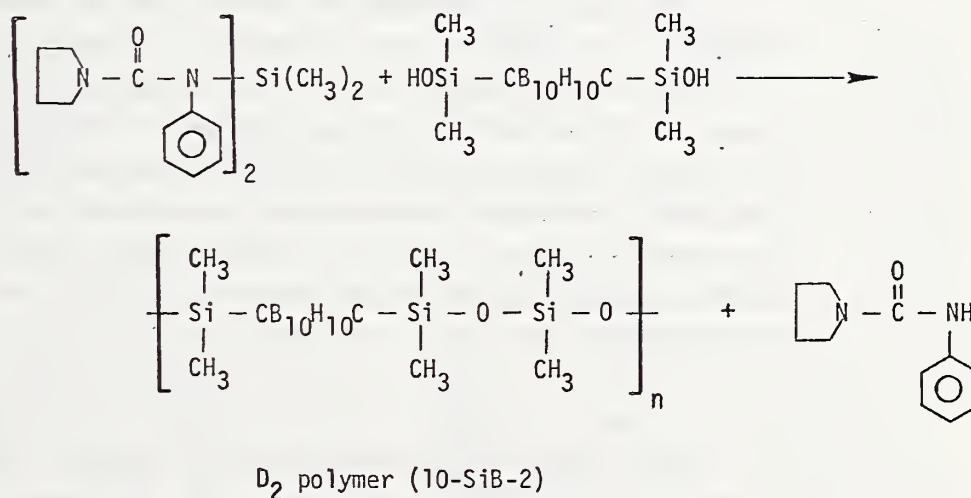
of the 10-SiB-1 polymer by alcoholic condensation (22) just as the  $C_{2}B_{10}$ -disilanol monomer does not undergo hydrolytic polycondensation (20). Apparently the influence of the  $C_{2}B_{10}$  cage inhibits scission of the Si-O, SiO-H, and/or SiO-R bonds on the monomer. Whether the reason is steric in nature or due to electron charge smoothing is not known, but the  $C_{2}B_{10}$ -disilyl monomer resists hydrolytic and alcoholic condensation. However,  $C_{2}B_{10}$ -monomers which contain additional siloxy groups corresponding to Dexsil 300 or larger undergo hydrolytic polycondensation in water/ether/THF solutions at 0°C, and linear polymers of 10-SiB-3 and 10-SiB-5 were first prepared in this manner (23). All of the 5-SiB polymers also can be prepared with this technique.

The experimental procedure involved the addition of water/THF to a solution of the appropriate monomers dissolved in ether. The reaction flask is maintained at 0°C during the addition and then allowed to warm to room temperature and digested for another 2-1/2 hours. The solvents are stripped off by relatively low temperature (30-35°C) evaporation under vacuum conditions. This procedure was found to eliminate the problem of crosslinking during synthesis, and soluble (linear) 10-SiB polymers with average molecular weights in the 10,000 range and peak maxima around 16,000-20,000 were first produced in this manner. Copolymerization of these same monomers with phenylated silanes produced the appropriate phenylated polymers.

Acid-Catalyzed Polycondensation of Diols. The OH-terminated counterpart of the chloro-monomer that was used successfully to synthesize Dexsil 300 by hydrolytic condensation was found to undergo acid-catalyzed condensation at elevated temperatures (23). The OH-terminated monomer was first prepared by treatment of the chloromonomer with sodium bicarbonate in moist ether. Polymerization was then effected by heating the monomer for 20 minutes at 200°C and 4 hours at 170°C in vacuo in the presence of a catalytic quantity of  $H_2SO_4$  (~0.6 wt-%). In this synthesis the 170°C temperature did not induce formation of a crosslinked gum. The Dexsil 300 polymer produced had a molecular weight distribution comparable to that produced by the hydrolytic condensation method. The peak maximum was at MW = 16,000-20,000.

High Molecular Weight  $C_2B_{10}$ -Based Polycarboranesiloxanes. Of the various methods for synthesizing the polycarboranesiloxanes prior to a few years ago, none produced polymers with molecular weights exceeding 100,000, and then only rarely. Generally, the molecular weights were between 5,000 and 20,000 and consequently possessed poor tensile properties. The reasons, in retrospect, were undoubtedly due to a combination of factors such as lack of high monomer purity, incomplete conversion, and, with copolymer systems, non-precise stoichiometry, as elaborated in Section VI.

At Union Carbide the challenge of fabricating high molecular weight polycarboranesiloxanes was met by reacting the disilanol of the  $C_2B_{10}$ -silyl monomer with difunctional silanes having appropriate facile leaving groups ( ). A variety of silanes were investigated, but certain ureido-silanes were found to be particularly attractive because they were non-basic and formed insoluble urea byproducts, which led to high conversions. A typical polymerization reaction, utilizing an N-pyrrolidine derivative, is as follows:



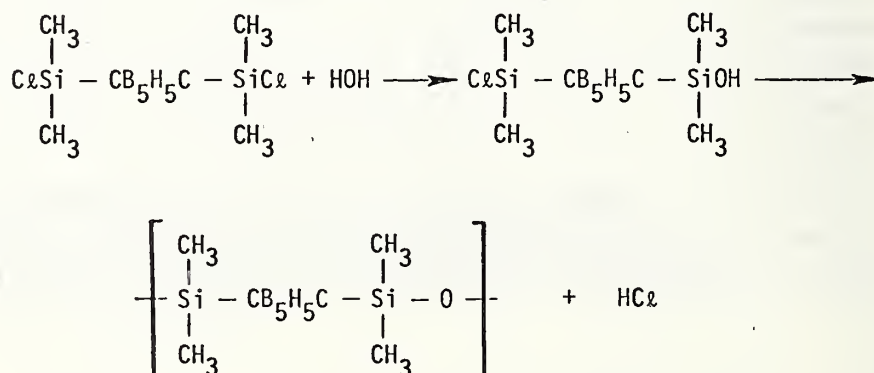
Linear polymers with weight average molecular weights as high as 250,000 (720 repeating units, 1440 chain units) have been synthesized in this way. Furthermore, substitution of 33 mole percent of either

diphenylsiloxane or methylphenylsiloxane moieties in the chain produced an amorphous polymer suitable for elastomer formulations.

Experimentally, the carborane monomer is converted to the diol by hydrolysis, then the ureidosilane (powder) is slowly added to the diol which is dissolved in chlorobenzene and maintained at 0 to -10°C. Reaction stoichiometry is carefully monitored by nmr, and on completion of the reaction the insoluble byproduct is removed by filtration.

High Molecular Weight C<sub>2</sub>B<sub>5</sub>-Based Polycarboranesiloxanes. Linear polymers of C<sub>2</sub>B<sub>5</sub>-carborane with molecular weights in excess of 10,000 were rarely achieved by the previously discussed methods, again most likely due primarily to impurities in the form of chain terminating trimethyl compounds. Recently at Chemical Systems high purity monomer, purified by repeated distillations on a spinning band column, was prepared and polymerized by hydrolytic condensation into the 5-SiB-1 homopolymer. The product was a linear polymer with  $\bar{M}_w = 182,000$ .

The preparation involved the slow addition of a water/dioxane solution to a vigorously stirred solution of the monomer also dissolved in dioxane at room temperature. The water was precisely measured to react to a 1:1 molar ratio with the monomer. Stirring was maintained for several additional hours, and then the temperature of the solution was slowly increased to dioxane reflux temperature (101°C) to induce polycondensation and drive off HCl formed in the reaction. The pressure was then reduced and the dioxane removed by distillation. The reaction is as follows:



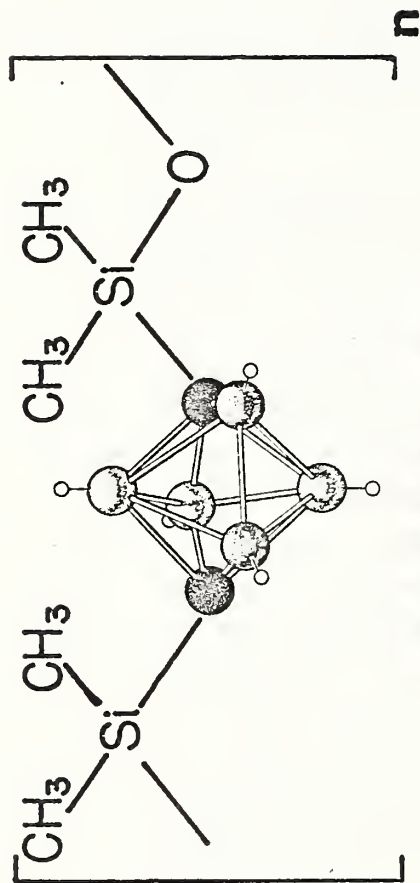


## VIII. POLYCARBORANESILOXANE CHARACTERIZATION

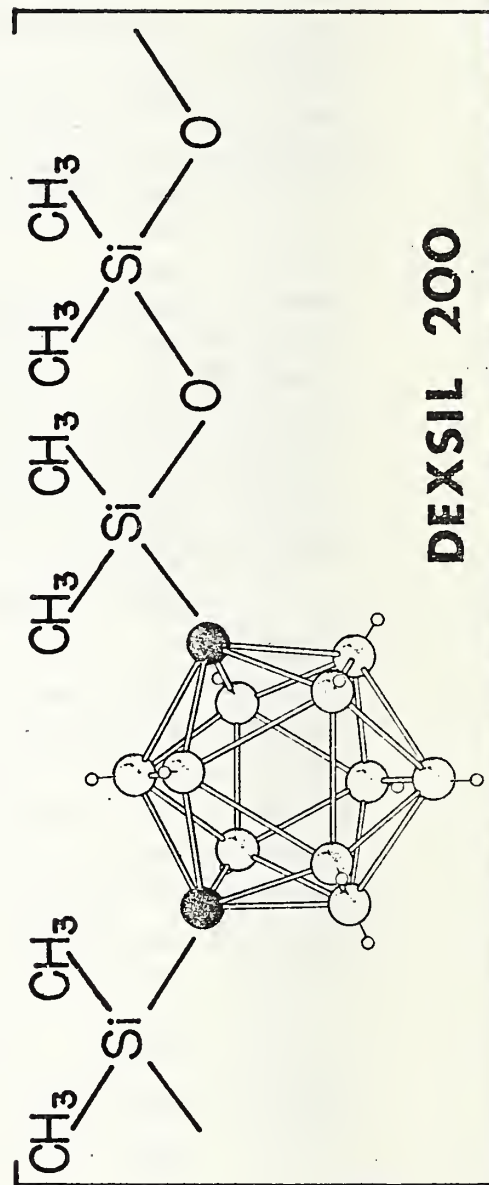
The polycarboranesiloxanes constitute a class of outstanding heat resistant polymers. In Fig. 9 are two members of this family of compounds, one (5-SiB-1) based on the  $C_2B_5H_7$  carborane and the other (10-SiB-2) based on  $m-C_2B_{10}H_{12}$  carborane. Structurally, these polymers can be visualized as silicones with bis-silylated carborane units inserted in the chain. In an ordinary silicone, and this holds for silicates in general, the Si-O-Si bonds develop substantial double bond resonance character due to a shift of the extra electrons on oxygen toward silicon and their accommodation in the unfilled 3d orbitals of the silicon atoms (13). The bonds are shorter and stronger and the angles are wider than would be anticipated by simple addition of atomic radii. The weakly electron-donating methyl groups also contribute to strengthening of the Si-O bonds but at some sacrifice in the strength of the Si-C bond. The decreased electron density at the methyls, however, makes them less reactive, particularly toward electrophilic reagents and free radical attack by oxygen molecules, at least compared with hydrocarbons. The methyl groups, as might be expected, are the most vulnerable points in the polymer. If, now, carborane moieties are interspersed along the chain, there must be a further delocalization of electrons in the form of a shift toward the electron deficient carborane cage. This strengthens in particular the bond between the cage-carbon and the silicon, but it must also further diminish the activity of the methyl groups because the stability of the polymer increases dramatically. The methyl groups remain the points of greatest vulnerability, thermally and oxidatively, but the activation energies for the reactions have to be significantly greater than in silicones. The stabilities of these compounds are apparent in characterization studies, such as thermal gravimetric analysis (TGA), torsional braid analysis (TBA), modulus temperature measurements, etc. as well as by spectroscopic analyses of degradation products formed by various temperatures.

Thermal Gravimetric Analyses. TGA curves give dramatic testimony to the heat resistant characteristics of the polycarboranesiloxanes. Figs. 10 and 11 show typical weight changes as functions of temperature

Figure 9. Examples of Poly-carboranesiloxanes - a 5-Sib-1 and a 10-Sib-2



PENTASIL 10



DEXSIL 200

FIGURE 10

# THERMAL GRAVIMETRIC ANALYSIS

PENTASIL POLYMERS

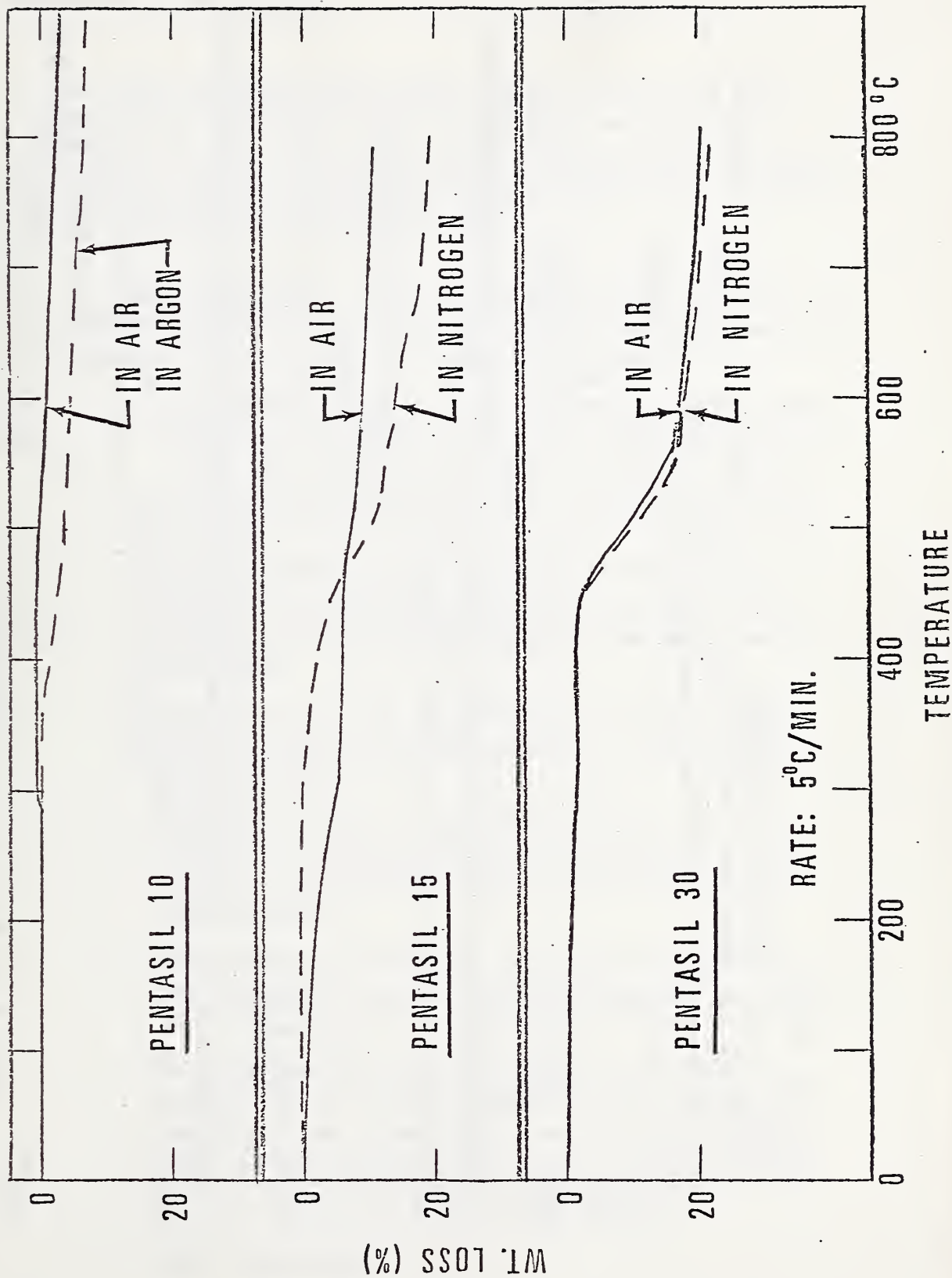
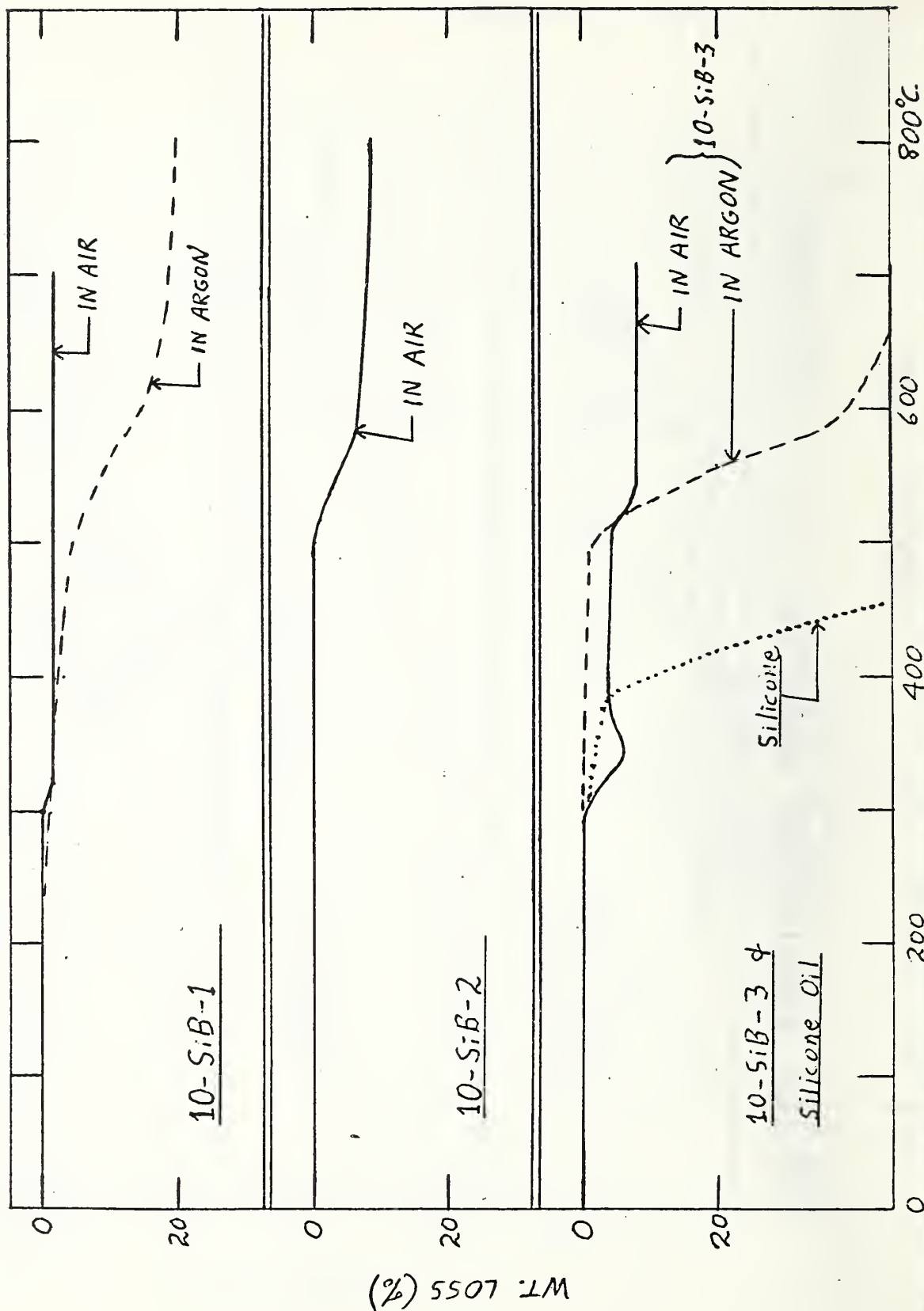


FIGURE 11  
TGA's OF DEXSIL POLYMERS





for various 10-SiB and 5-SiB polymers. Particularly with SiB-1 compounds and in the presence of air, the TGA curves are practically straight lines up to 500°C and very little change thereafter. Silicone polymers, by way of comparison, begin to lose weight as low as 200-300°C and by 350-400°C the losses become severe.

Evaluation of Data. All of the various techniques, TGA, DSC, TBA and spectroscopic evidence by which the Dexsil and Pentasil polymers were characterized brought out the following salient points:

- The thermal stability of a polycarboranesiloxane is an inverse function of the number of siloxy groups in the repeating unit, as indicated by weight loss observed in TGA. Mass spectral analysis supports this relationship by showing the cyclizing groups split out of the chain in the higher SiB formulations.
- The methyl groups in the polymer are the points of greatest vulnerability, oxidatively and thermally, and the farther removed they are from the carborane cage, the more vulnerable they become.
- Thermally, for a given SiB formulation, there appear to be little differences between the stabilities of Pentasil and Dexsil polymers.
- Thermo-oxidatively, for a given SiB formulation, a Dexsil is somewhat more stable with respect to the value of  $T_{ox}$  than a Pentasil. 10-SiB-3 shows about the same resistance to oxidation as 5-SiB-1.
- Polymers in inert environments can withstand temperatures substantially higher than in oxidative environments. The differences are generally on the order of 100° to 150°C.
- The SiB-1 formulation, both for  $C_{2}B_{10}$  and  $C_{2}B_{5}$  polymers is extremely stable once it has been oxidatively crosslinked. The TGA's of these polymers in air are practically straight lines, showing very little gain or loss of weight. This behavior is of practical importance in coatings.

- A  $C_2B_5$  polymer for a given SiB formulation is more tractable than a  $C_2B_{10}$  polymer, i.e., it has a lower  $T_g$  and a lower  $T_m$ .
- The addition of small concentrations of silicon-pendant phenyl groups improves the thermal and oxidative resistance of the Dexsil polymers significantly. Dexsil 400 $\phi_1$  is more stable than unmodified Dexsil 300 despite the fact that it has one more siloxy group in the chain.
- Proper compounding and curing improves oxidation resistance tremendously. Without compounding or curing, the polycarborane-siloxane resins begin to crosslink oxidatively in the 270-300°C region. With silica and iron oxide fillers and peroxide curing,  $T_{ox}$  can be raised 45-50°C.
- Para-carborane polymers are somewhat more temperature resistant than meta-carborane polymers in that weight losses in TGA occur at somewhat higher temperatures. However, the total weight loss that occurs up to 800°C is about the same for both polymers. Also, the para-carborane polymer has a disadvantage in having a higher  $T_g$  and  $T_m$ .
- The polycarboranesiloxanes are considerably more stable, oxidatively and thermally, than pure silicones.
- High molecular weight polycarboranesiloxanes with good tensile strengths can be prepared by careful attention to monomer purity, precise co-monomer ratios, and high conversion percentages for the transition of monomers into polymer.

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POLYELECTROLYTE MOSAIC MEMBRANES: PART II

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## ABSTRACT

Piezodialysis is a unique mode of ion transfer through a membrane. When a saline solution is forced to flow through a piezodialysis membrane, the net flow of ions through the membrane exceeds the volume flow of water so that the permeate becomes enriched and the feed becomes depleted in salt. Structurally, a piezodialysis membrane consists of a mosaic of alternating microdomains of cation and anion exchanging polyelectrolytes which preferably extend uninterruptedly from the top to the bottom surfaces, thus providing pathways for the cations and anions through the membrane.

Mosaic membranes have been fabricated in various ways, but one which we have found to be relatively simple as well as amenable to many modifications is made by a process called phase inversion. This consists of dissolving in a common solvent system a cation-exchanging polyelectrolyte and the precursor polymer of an anion-exchanging polyelectrolyte, both synthesized with suitable moieties that permit subsequent crosslinking, then casting this solution into a thin film and allowing the solvent to evaporate. At this point the polymers begin to precipitate, the first one forming islands in a matrix of the second. The membrane is then crosslinked by heating, and the precursor polymer finally is quaternized by a simple gas phase reaction. Exploratory membranes to demonstrate feasibility have been synthesized in this manner, and salt enrichment values up to 180% (ratio of brine water to product water) have been obtained.



## SECTION I

### EXPERIMENTAL

#### 1.0 PIEZODIALYSIS TYPE MASS TRANSPORT

If pure water is forced by pressure through an ion exchange membrane, e.g., one made of sodium polystyrene sulfonate, the movement of water forces the  $\text{Na}^+$  counterions in the membrane to begin to move in the direction of the water flow. The  $\text{SO}_3^-$  anion sites, however, are fixed in position and cannot move, so the  $\text{Na}^+$  ions can travel only a short distance before the attractive forces between the  $\text{Na}^+$  and  $\text{SO}_3^-$  inhibit further ion flow. There is a net charge differential,  $\delta^+$  at the bottom of the membrane and  $\delta^-$  at the top, due to the incremental displacement of the  $\text{Na}^+$  ions. This is the well known *streaming potential* and is illustrated in Figure 1.

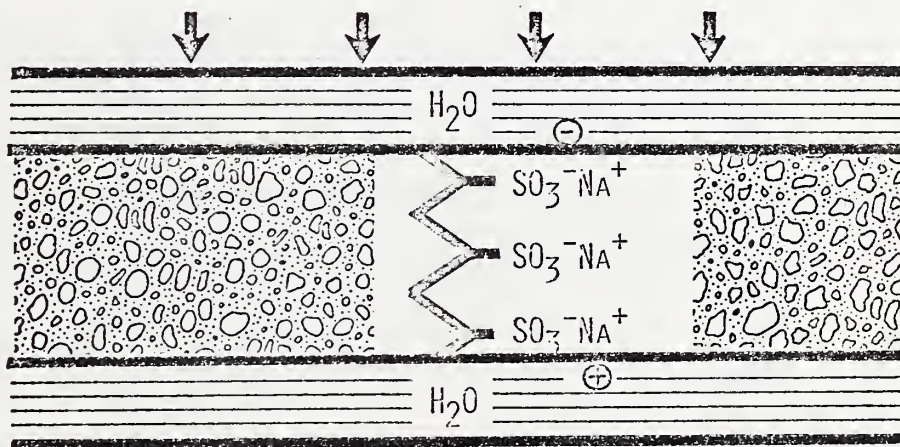


Figure 1. Streaming potential in an ion exchange membrane.

If a saline solution is then substituted for the pure water in Figure 1, the  $\text{Na}^+$  counterions in the membrane will again begin to move through the membrane at the onset of flow, but now there are  $\text{Na}^+$  ions in the feed to occupy the vacated sites in the membrane. The  $\text{Cl}^-$  ions in the feed solution, however, are restrained from moving into the membrane by the fixed  $\text{SO}_3^-$  sites and by the streaming potential in the membrane. These forces act to retard further flow of counterions so that both  $\text{Na}^+$  and  $\text{Cl}^-$  are inhibited from moving through the membrane. Consequently, if the water continues to flow, the feed water becomes enriched in salt and the permeate becomes depleted (Figure 2).

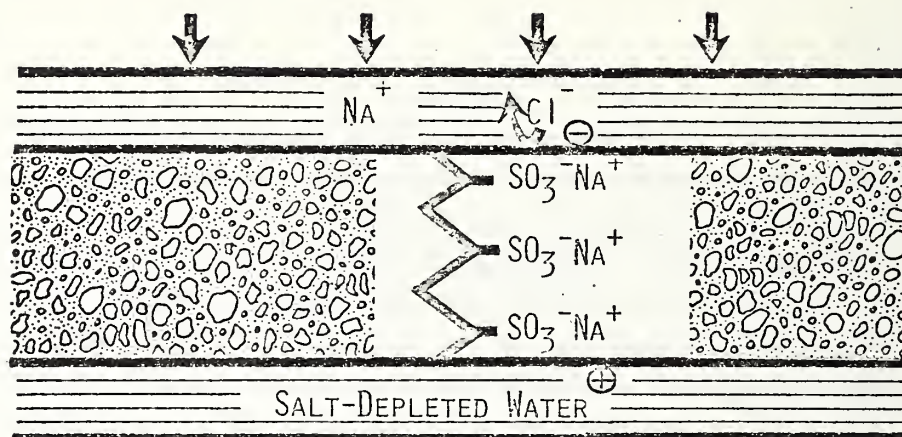


Figure 2. Salt rejection by an ion exchange membrane.

The effectiveness with which a given ion exchange membrane excludes coions determines its salt rejection capabilities, and rejections on the order of 50-60% are readily attainable.

If now instead of a simple monofunctional ion exchange membrane we substitute one having alternating patches or domains of anion and cation exchanging polyelectrolytes, there will then be pathways for both the  $\text{Na}^+$  and the  $\text{Cl}^-$  ions (Figure 3), and these ions will continue to move stairstep fashion into and through the membrane as long as they are neutralized and

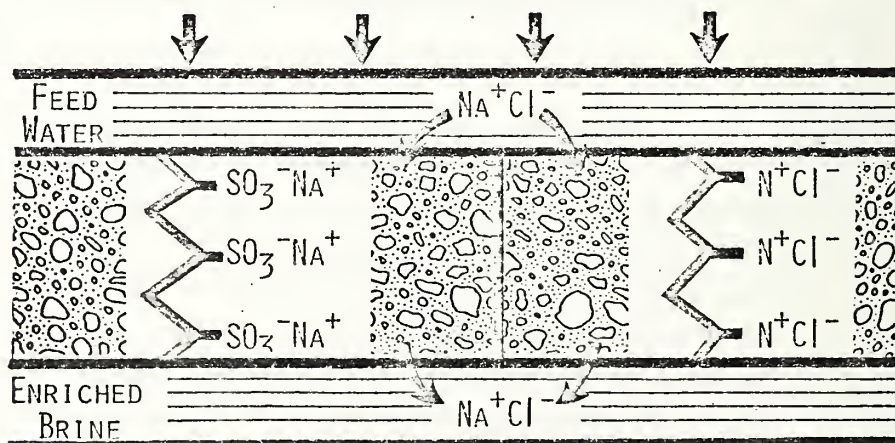


Figure 3. Salt enrichment by piezodialysis.



dispersed at the bottom surface. It is important to realize that the net flow of salt through the membrane under these circumstances is greater than the flow of water. The feed water, after salt depletion, becomes the product, while the salt-enriched filtrate becomes the brine, or permeate.

A membrane of the type shown in Figure 3 is known as a *mosaic* membrane, while the ion transport process is termed *pressure* or *piezodialysis*. For piezodialysis to occur there are a number of requirements and important factors to be considered.

- Pressure is the driving force which, by moving water through the membrane, creates the charge imbalance and causes piezodialysis action to occur.
- The charge domains should extend uninterruptedly from the top surface to the bottom. Within the membrane itself, electrical neutrality is preserved between the fixed ion sites and the counterions regardless of conditions outside the membrane, so the pathways for the counterions can be devious—so long as they are not discontinuous. If the ion in its movement through the membrane encounters a discontinuity in the form of an adverse polyelectrolyte, it may cease flowing, causing localized salt rejection at that point.
- Adjacent domains should be in sufficiently close proximity at the membrane's surfaces to provide charge neutralization in the solutions (feed and brine) and prevent buildup of a streaming potential within a given domain. Dead space between domains should be minimal.
- The smaller the domains, the higher the mass transport of ions because the centers of large domains are not as effectively neutralized as the edges and hence can carry less ion flow, or current. However, there is also a lower limit because along the interfaces between domains the polyelectrolyte fixed sites will tend to neutralize one another and will not be able to transport counterions. The optimum size has not been determined, but it is generally believed to be somewhere between 0.01 micrometers (100 Angstroms) and 1.0 micrometers.

Piezodialysis-type flow in a mosaic was first predicted in 1932 by Sollner [1]. Transport theories were developed by Kedem and Katchalsky [2] and later greatly embellished and refined by Weinstein [3], by Dresner [4], and by Leitz [5], and their respective coworkers. At the onset of our program (August, 1972) experimental feasibility of desalination by piezodialysis action through mosaic membranes had already been demonstrated by Weinstein [3b] and Leitz [5], utilizing various configurations such as ion

exchanger patches embedded in silicone, polyelectrolyte/latex strips, etc. Our initial approach [6] involved the synthesis of mosaic membranes utilizing ionotropic gels [7-13] as templates on which to structure the mosaics. In the micro-capillaries of the gel, an SEM photo of which is shown in Figure 4, was inserted one of the polyelectrolytes; in the matrix (which is 98% water in the nascent gel) the water was replaced by the other polyelectrolyte. Fabrication was possible on a very small scale, where the specimens could be sliced to remove overlying surface films, but on a larger scale the approach was fraught with difficulties. One of the polyelectrolytes always seemed to spread out on the surface, which is disastrous because even an ultrathin film of one polyelectrolyte causes salt rejection (Figure 2). Work on this approach was set aside when it was found the mosaic membranes could be made more practically by a phase inversion technique, as described below.

### 1.1 PHASE INVERSION TECHNIQUES

If an appropriate viscous solution consisting of a polymer, a swelling agent, and a volatile solvent is cast as a membrane, the polymer and the swelling agent, because of solubility differences, will separate into domains as the solvent evaporates [14]. If the swelling agent, which is a nonsolvent for the polymer, is then removed either by evaporation or by leaching, the membrane becomes perforated. Under the right set of solubility and volatility conditions the perforations will be in the size range desirable for piezodialysis type membranes. The first test of the feasibility of this approach [15] involved fabrication of a crude but porous phase inversion membrane formed by dissolving equal amounts (4.25% of each by weight) of polyvinylalcohol and poly(2-methyl-5-vinylpyridine) in an organic solvent, then casting the viscous solution as a 10-mil thick membrane. After drying, the membrane was washed with water to remove the polyvinylalcohol. The leached membrane is shown in Figure 5, wherein the white spots are the vacancies which had previously contained the polyvinylalcohol. The domains are on the order of 20-30 micrometers in diameter.

A porous membrane also can be produced by using a volatile swelling agent in place of the non-volatile polyvinylalcohol. The sequence of events is: (a) the highly volatile solvent evaporates quickly, as soon as the film is cast; (b) as the solvent evaporates the polymer and swelling agent begin to drop out of solution; (c) the polymer and swelling agent, if sufficiently incompatible, coalesce and form separate domains; and (d) the swelling agent



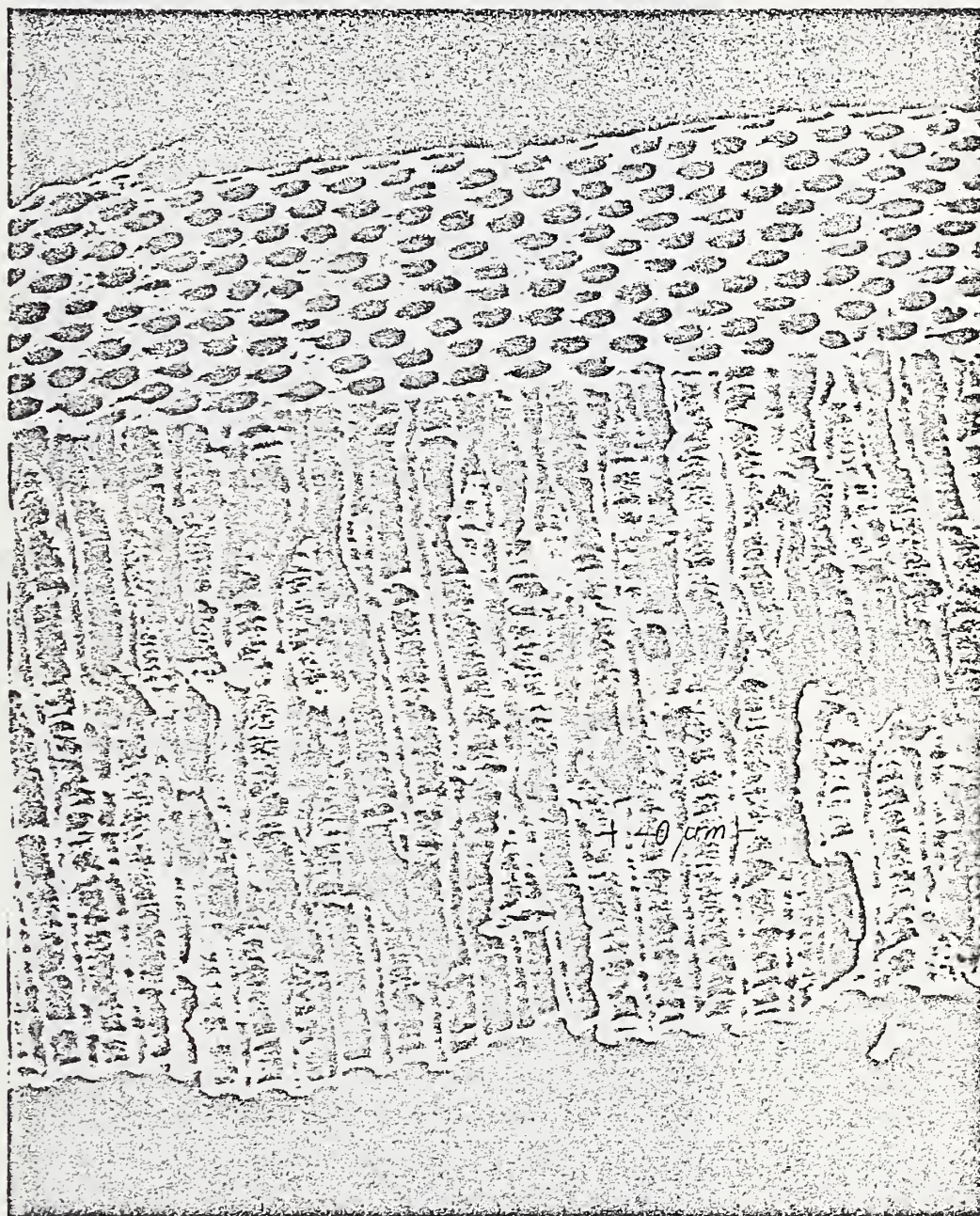


Figure 4. SEM photomicrograph of a cross-section of an ionotropic gel membrane.

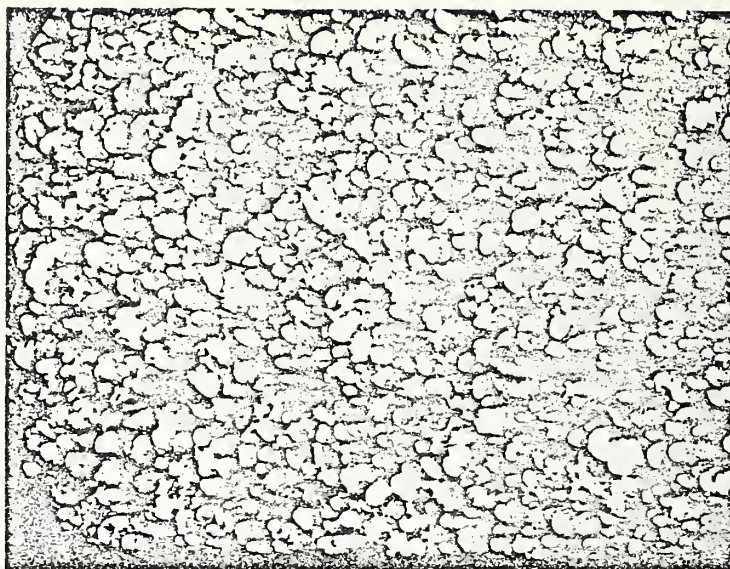


Figure 5. Phase inversion membrane formed by casting a solution containing polymeric 2-methyl-5-vinylpyridine and polyvinylalcohol (PVA) followed by leaching with water. White spots indicate prior location of PVA domains. 100X.

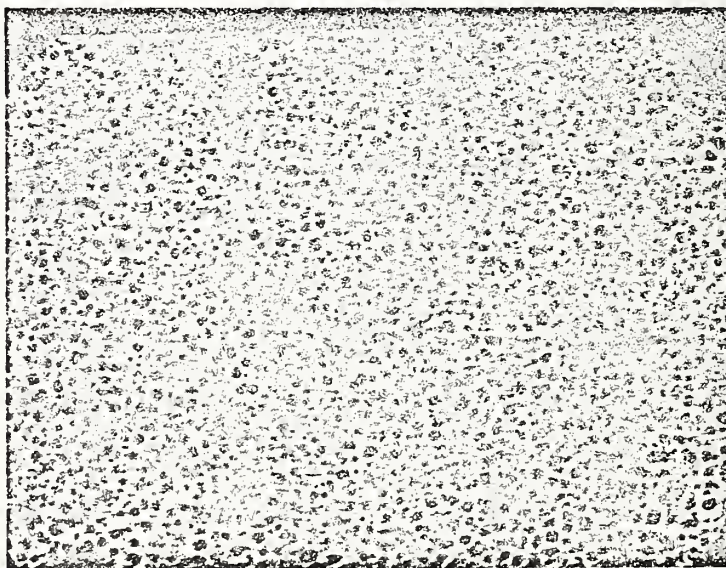


Figure 6. Phase inversion membrane formed by casting polymeric 2-methyl-5-vinylpyridine in a solution containing a volatile ether. The pores are very similar in magnitude to those of the ionotropic gels. 100X.



evaporates, leaving holes in the film. Figure 6 shows a polyvinylpyridine membrane cast with a volatile ether as swelling agent and methylene chloride as solvent. The capillary pores are on the order of 5-10 micrometers in diameter.

Now, if the roles of organic polymer and swelling agent cited in the previous examples could be taken by two suitable polyelectrolytes, then the cast film would be transformed simply and directly into a piezodialysis mosaic membrane as phase separation occurred in the film, as the solvent evaporated. This would indeed be a significant achievement if it could be done. Polyelectrolytes, however, do not cooperate that readily, for in a solution of two opposite polyelectrolytes the fixed ion sites on one tend to be neutralized by the fixed sites on the other, which in turn leads to precipitation of both components from solution. It is possible to circumvent this problem, however, by using only one polyelectrolyte in the casting solution; the other exists as its organic precursor polymer, which is transformed into the counterpart polyelectrolyte after the film has been cast and the domains are locked in place. This is the approach that has been followed during the past several months at Chemical Systems.

## 1.2 FABRICATION OF MEMBRANES

### 1.2.1 Selection of Polymers and Solvents for the Casting Solution

A wide variety of cation and anion exchanging polyelectrolytes exist, but for initial experiments where feasibility was the first consideration the choice was sodium polystyrene sulfonate and poly(1,2-dimethyl-5-vinylpyridinium chloride) because their monomers are readily available and are amenable to a wide variety of copolymerization reactions. Because of the incompatibilities discussed in the previous section, only one polyelectrolyte can be tolerated in the casting solution; the other component must be the precursor polymer for the other polyelectrolyte. Since quaternization is a relatively simple treatment compared with sulfonation, the decision was made to use sodium polystyrene sulfonate as polyelectrolyte and poly(2-methyl-5-vinylpyridine) as the precursor in the casting solution.

The first problem encountered with the above polymer combination was the selection of a solvent or solvent combination that would dissolve both polymers. The P(SSS) is soluble only in water, at least to the degree

required for membrane casting, while the other polymer, P(2M5VP), is soluble only in organic solvents. Since one solvent must be water, the other obviously must be compatible with water, preferably miscible, and must also be a good solvent for P(2M5VP). Since the mosaic pattern is created as the two solvents evaporate, their volatilities should also be reasonably close together. Candidate solvents therefore had to include compounds such as low molecular weight alcohols, acetone, dioxane, certain ethers (tetrahydrofuran) etc.

The various solvent combinations were studied, and the best one was found to be methanol/water in the approximate ratio of 3:1. The casting solutions were made up by dissolving known concentrations of the two polymers in their respective solvents, then mixing the two solutions together in the desired proportions. The casting solution should be highly viscous but still amenable to casting with a doctor blade.

#### 1.2.2 Crosslinking Techniques

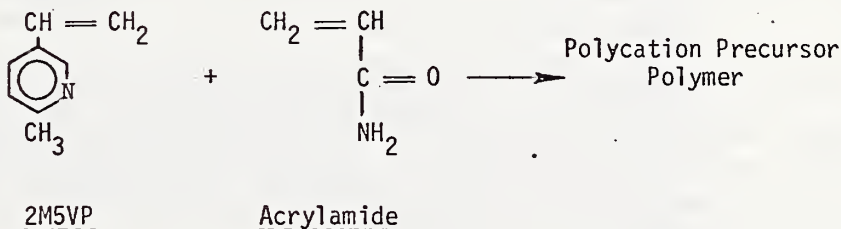
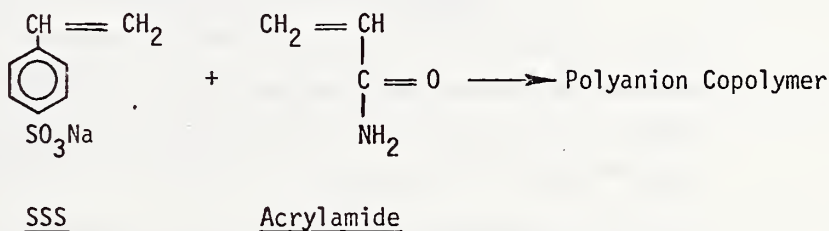
Once the membrane has been cast and the two polymers have agglomerated into their separate micro-domains, the next problem is to lock the polymers in place so that later, when in contact with water, they cannot fuse together and neutralize one another, cannot leach out, and cannot swell to the point where the membrane would wrinkle excessively or break loose from its support. Initially attempts were made to crosslink the sulfonate polymer ionically by treatment with barium chloride (barium sulfonate is insoluble), but the domains were destroyed by the aqueous solution. Barium chloride powder did not work either. Copolymers of SSS and 2M5VP with methacrylic acid were then synthesized, and crosslinking attempts with hexane diamine and hexanediol were made. Again, however, it was found that the treatment destroyed the domains. The crosslinking agents were organic liquids, and unfortunately they dissolved the vinylpyridine polymer before crosslinking reactions were initiated.

The lack of success by these techniques then dictated the need for crosslinking by non-destructive treatments, either by radiation (e.g., ultraviolet light) or by gas phase reactions which would not destroy the domains. Hence, pendant functional groups such as vinyls, amines, methylol, or any others amenable to crosslinking by these techniques, had to be included in

the chains. Crosslinking through vinyls could be effected by ultraviolet radiation, through amine groups by reaction with gaseous formaldehyde, through methylol groups by reaction with gaseous  $\text{HC}\ell$  or by simple heating, etc.

After considerable preliminary experimentation, two successful crosslinking techniques that worked for both the polyanion and the polycation chains were devised. These were:

Formaldehyde/Amide Crosslinking — This involved the reaction of formaldehyde with pendant amide groups that had been incorporated into the polymers by appropriate copolymerization of the primary monomers with acrylamide, i.e.,



As discussed later, crosslinking occurs when the amide is reacted with the formaldehyde—after the membrane is formed.

Free Radical Initiated Crosslinking — This involved crosslinking through pendant vinyl groups that had been incorporated into the chains by copolymerization of the primary monomers with butadiene, completely analogous to the previous equations except that butadiene was substituted for acrylamide. Successful crosslinking was effected through pendant vinyls by adding an initiator and then heating.

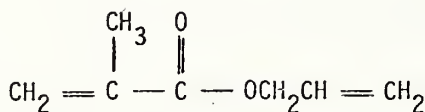


In addition to the foregoing successful methods, there were numerous unsuccessful attempts at crosslinking. In chronological order the various methods are discussed below.

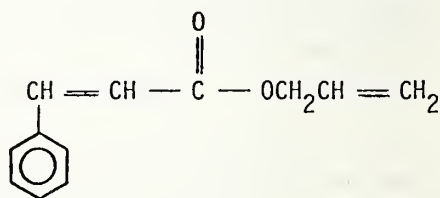
1.2.2.1 Ultraviolet Crosslinking with Butadiene Copolymers — Copolymers of butadiene (BD) with sodium styrene sulfonate (SSS) and of butadiene with 2-methyl-5-vinylpyridine (2M5VP) were synthesized, the first by emulsion polymerization and the second by solution polymerization. In copolymers of these types a significant number of pendant vinyl groups occur because chain propagation through the first vinyl in the molecule occurs with greater facility than through the second vinyl.

The P(2M5VP-BD) films were found to be amenable to crosslinking by u.v. irradiation, particularly when benzophenone initiator was added. Films of P(SSS-BD), however, could not be crosslinked, not even with benzophenone. Water interferes with ultraviolet-induced reactions, so in this case hydration of  $\text{SO}_3^-$  probably prevented crosslinking.

1.2.2.2 Crosslinking with Acrylate and Cinnamate Copolymers — Two approaches have been utilized to try to crosslink the polymers by incorporating acrylate and cinnamate molecules in the polymer chains. The first approach consisted of assimilation of the allyl ester in the chain during polymerization, while the second involved synthesis of copolymers with pendant hydroxyl groups, to which could then be attached the appropriate unsaturated moieties. In the first approach copolymers of both SSS and 2M5VP were synthesized with difunctional vinyl monomers, i.e., with allyl methacrylate and allyl cinnamate.

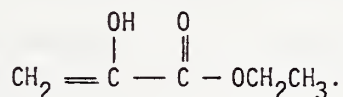


Allyl methacrylate

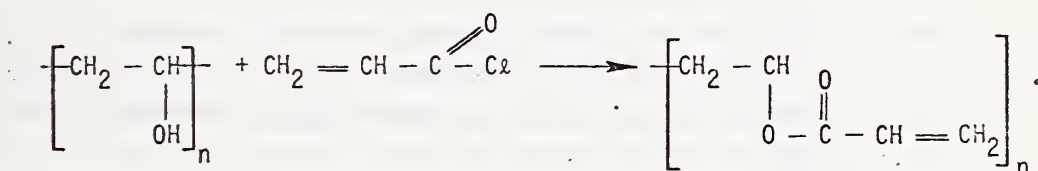


Allyl cinnamate

The polymerization reaction is supposed to occur primarily through only one of the unsaturated linkages of each co-monomer, leaving the other as a pendant group available for crosslinking. However, all attempts to crosslink them, either in bulk or in the membrane, failed. The second approach, utilizing reactions between hydroxyl pendant groups and unsaturated chlorides, was partially successful. Copolymers of vinylacetate with SSS and with 2M5VP were synthesized with no problems, and the acetate was easily hydrolyzed with an aqueous acid to give OH functionality on the chain; likewise, copolymers of SSS and MVP also were easily made with 2-hydroxyethylacrylate.

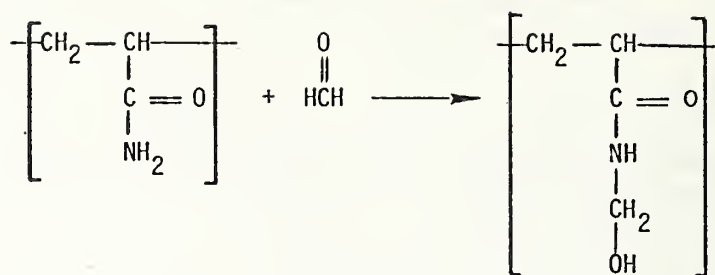


The esterification of P(MVP-vinylalcohol), carried out in tetrahydrofuran, occurred readily, as follows,

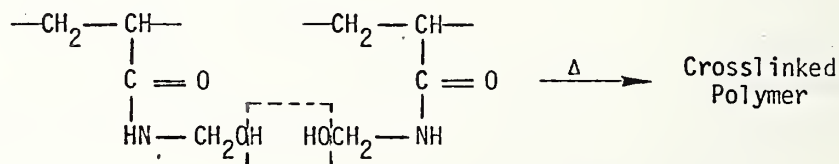


and films were actually cast and successfully crosslinked with ultraviolet. However, esterification of P(SSS-vinyl alcohol) presented problems because water is the only adequate solvent for the polyelectrolyte, whereas the anhydrous chloride must be kept away from water. The reaction was therefore run in formamide, which affords limited solubility of the polymer, but the reaction was not particularly successful. Synthesis of the p-toluidine salt of PSSS would seem to offer one way around the solubility problem, but past experiments had indicated that the p-toluidine salt protonates the nitrogen in the vinylpyridine ring of P2MVP. Tetraalkyl ammonium salts probably could be used in this situation, but a more promising route to crosslinking, viz., acrylamide copolymers, was discovered, so the pendant vinyl approach was set aside.

**1.2.2.3 Crosslinking via Acrylamide Copolymers** — Copolymers of acrylamide with SSS and with 2M5VP were synthesized with the idea of crosslinking through the amide groups by reactions with gaseous formaldehyde. The first step would be formation of the N-methylolamide:



The second step, crosslinking, would occur by splitting out water:



This technique was carried out successfully with both the P(SSS-acrylamide) and P(MVP-acrylamide) in mosaic membranes. The membrane can be simply placed in a closed container along with paraformaldehyde and heated at 160°C for several hours or, alternatively, basic formalin solution containing  $\text{K}_2\text{S}_2\text{O}_8$  initiator can be included in the original casting solution. In addition to crosslinking internally within a domain, this technique allows polymers to crosslink across domains, thereby greatly improving surface integrity. The amide also contributes to the adhesion of the mosaic film to the supporting polyester paper, and the final product consequently has outstanding physical strength and flexibility.

A variation of the amide/formaldehyde linkage consists of synthesis of the methylol derivative of each of the two bulk polymers by gentle treatment with formaldehyde prior to casting. After casting, the membrane is simply heated to induce crosslinking. The advantage lies in the fact that post-treatment is simplified; the disadvantage is that some crosslinking inevitably occurs in the bulk phase prior to casting. A further modification is to treat the methylol moieties in the membrane with gaseous  $\text{HCl}$ , which catalyzes the crosslinking reaction. This reaction is generally unsatisfactory, however, because protonation of the nitrogen in the pyridine ring occurs first, causing the PMVP to become soluble in the water present in the membrane and thereby immediately destroying the domains by combination with the polyanion.

1.2.2.4 Free Radical Crosslinking Through Unsaturated Moieties — As discussed in the next section, membranes made from polyelectrolytes crosslinked by the acrylamide/formaldehyde reaction were the first successful phase inversion piezodialysis membranes. Free radical-induced crosslinking of butadiene-containing polyelectrolytes was then re-investigated, and it was found that simple heating of the membranes (with an initiator) at about 150°C for slightly over an hour was sufficient to produce a well-crosslinked membrane. This is in marked contrast to ultraviolet radiation, which had been unsuccessful in inducing crosslinking in SSS polymers. The free radical crosslinked butadiene-containing membranes had good physical properties and negligible swelling tendencies. Moreover, subsequent testing showed that salt enrichment values for these membranes were superior even to those of the acrylamide-containing membranes.

#### 1.2.3 Quaternization Reaction

The quaternization of polymers of 2-methyl-5-vinylpyridine with alkyl halides is a fairly easy task. The order of reactivity with methyl halides is iodide > bromide > chloride. The iodide goes at room temperature, while the chloride proceeds readily at temperatures of about 60°C (gas phase reaction). The presence of other moieties in the chain does not appear to inhibit the reaction.

The membranes discussed in the previous section were generally quaternized by heating in the presence of methyl chloride at 85°C for about two hours. Calibration experiments involving weight changes in a known quantity of P(2M5VP) on a membrane indicated that the above conditions were adequate for complete quaternization.

#### 1.3 DESALINATION TESTS

A large number of membranes were tested for their desalination capabilities, but those demonstrating piezodialysis action were all fabricated from one or the other of the following systems:

- a) Poly(sodium styrene sulfonate/acrylamide) + poly(2-methyl-5-vinylpyridine/acrylamide); crosslinked with formaldehyde, either in gas state or in formalin (in initial casting solution).
- b) Poly(sodium styrene sulfonate/butadiene) + poly(2-methyl-5-vinylpyridine/butadiene); crosslinked by heating; free radical initiator.



The casting solutions were prepared by dissolving the particular copolymers in separate solvents, then combining the solutions. For example, the P(2M5VP-AA) is dissolved in methanol and the P(SSS-AA) in water, and these were combined to make up a casting solution in which the methanol/water ratio would be about 3:1 by weight, while in the final mosaic membrane there would be approximately equal volumes (to produce equal domains) of the two polyelectrolytes. The acrylamide concentration in each of the two polymers would be about 30 mol percent because it had been found that this concentration produced domains that were on the order of 1-3 micrometers in diameter. A variation on this system involved the addition of butadiene polymer as a filler, which served to tighten the membrane, remove holes or other defects, and generally decrease the water flux through the membrane.

After the solutions were made up they were cast as films, either on glass plates for microscopic examination, or on porous polyester paper for desalination testing. The solvents were allowed to evaporate for 15-20 minutes, then sections of the cast membrane were crosslinked. With formaldehyde crosslinking, the membranes were heated in a closed container for several hours at 160°C in the presence of paraformaldehyde or, alternatively, the same procedure but with formalin in the casting solution. Butadiene copolymers were crosslinked by the same procedure (160°C oven) except that azobis-isobutyronitrile initiator was used in place of the formaldehyde treatment.

The crosslinked membranes were then quaternized at 85°C in an atmosphere of gaseous methyl chloride for about two hours. From calibration experiments based on weight changes in the membrane, it had been determined that the above conditions were sufficient for quaternization of the nitrogen in the pyridine ring.

The apparatus for desalination testing consisted of an Amicon high pressure cell equipped with a magnetic stirrer in the feed water section. Salt concentrations in the feed and product water were determined by conductivity measurements and checked by chloride ion analysis, using silver nitrate with potassium chromate indicator. The feed water was .01N in NaCl (580 ppm), and the highest enrichment achieved was 180% based on the ratio of salt in the permeate (brine) to that in the depleted feed water. The test data are shown in Table 1. The 180% enrichment value is comparable to values reported by Leitz [16] for latex membranes and by Yamabe, *et al* [17], for styrene-butadiene membranes.

TABLE 1  
Experimental Test Data

Polymer Systems:		A - P(SSS-Acrylamide) + P(2M5VP-Acrylamide)
		B - P(SSS-Butadiene) + P(2M5VP-Butadiene)
Solvent Systems:		Methanol/Water (3:1)
Membrane:		Cast 4 mils thick on polyester paper
Feed Solution:		0.01N NaCl

Test	Polymer System	Crosslinking Treatment	Test Cell Conditions	
			Pressure	Flux
#1	A	Paraformaldehyde, heated 160°C	500 psig	136. gfd
#2	A	Paraformaldehyde + HCl gas, 160°C	200 psig	35. gfd
#3	A	Formaldehyde (30%) + NaOH + K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ***	240 psig	5.4 gfd
#4	A	Same as #3 plus polybutadiene filler	1400 psig	0.7 gfd
#5	B	Heating 160°C, ABBN initiator	1400 psig	1.9 gfd
#6	B	Same as #5, but with skin	1400 psig	.02 gfd

\* Enrichment defined as:  $\frac{\text{Salt conc. in permeate (brine)}}{\text{Salt conc. in depleted feed (product)}} \times 100$

\*\* Microscopic examination of membrane indicated that HCl had destroyed the domains.

\*\*\* Formalin solution included in casting solution.



## SECTION 2

### FUTURE WORK

#### 2.0 SCOPE OF THE PHASE INVERSION TECHNIQUE

The fabrication of piezodialysis type membranes by the phase inversion technique is actually a relatively simple procedure, once the polymer systems, swelling agents, etc., have been selected, synthesized and dissolved in a suitable solvent. The big advantage of the phase inversion method lies in the fact that the post-treatments of the membrane are minimal and relatively easy. Membrane preparation simply involves spreading the viscous casting solution into a thin film, allowing it to dry, then crosslinking it by heating or by a gas phase reaction, and finally quaternizing it by another gas phase reaction. Moreover, since the ultimate goal is to use the membrane in a large desalination element, e.g., a spiral wound module, then crosslinking and quaternization could be carried out very easily after the spiral wound element had been assembled. The element would be placed inside an oven and the requisite gases would be allowed to flow through it.

For laboratory experimentation, the phase inversion technique is extremely versatile in scope and offers unusual opportunities to modify parameters and change the membrane's structure and composition to optimize desalting characteristics. The following possibilities exist:

- Domain size — Can be varied by making changes in polymer molecular weights, by incorporating other moieties in the polyelectrolyte chain (e.g., acrylamide), by utilizing coupling agents (surfactants), or by using polymer grafting techniques.
- Porosity, flux — Can be increased by using swelling agents that leach out or will evaporate after the membrane is set; can be reduced by using fillers (e.g., polybutadiene), which eliminate defects and reduce porosity; flux can also be changed by changing membrane thickness.
- Asymmetric skin — Can be produced by increasing the vaporization rate of the solvent or by post-treating the membrane.
- Swelling — Can be varied by varying the amount of cross-linking.
- Strength, pliability, handling — Can be improved by adding other moieties (e.g., butadiene) in the chains; moderate improvements can be effected by adding a plasticizer (e.g., glycerol) which "lubricates" the membrane.

The previous discussions have been limited to flat sheet piezodialysis membranes, but there is no technical reason why they could not also be extruded as hollow fibers. The substantially larger surface area per unit volume of a hollow fiber desalination element versus a flat sheet, spiral wound element, gives it a significant advantage---about 25-fold. A fiber composed of polystyrene/polyvinylpyridine (butadiene copolymers) should have the requisite strength to withstand the pressures in a piezodialysis desalination system.

## 2.1 INCORPORATION OF AN ASYMMETRIC SKIN

The accomplishments that have already been achieved with exploratory type flat sheet membranes were discussed in Section 1.3, and even with these fairly primitive, relatively uncontrolled membranes enrichment values up to 180% were obtained. By careful variation of "one parameter at a time," if such is ever really experimentally possible, significant additional improvements in salt enrichment should be practically a certainty.

One of the important requirements for good piezodialysis action, as discussed in the background data in Section 1.0, is that the polyelectrolyte domains should extend from the top to the bottom of the membrane to provide continuous pathways for the transport of counterions. However, with a membrane that is 4 mils thick, which is close to minimal thickness for good handling characteristics, it is virtually impossible to produce domains that extend 100 micrometers (4 mils) through the membrane but which are only 1-2 (or preferably even less) micrometers in cross-section. The way around this problem, however, would seem to be to put a thin skin on the surface, i.e., fabricate a membrane, either flat sheet or hollow fiber, which has a thin asymmetric skin supported on a porous substructure, exactly analogous to the structure of reverse osmosis membranes. In this structure the asymmetric skin is the "working part" of the membrane, while the porous substructure merely supports the skin and is actually superfluous for the piezodialysis transport of ions.

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ELECTRICAL PROPERTY STUDIES OF PLANAR  
METAL COMPLEX SYSTEMS

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Abstract

The use of electrical property measurements to obtain information regarding the conduction process and intermolecular interactions in molecular solids containing planar metal complexes is discussed. The results of recent electrical conductivity and thermopower studies on the compounds  $\text{Pt}(\text{NH}_3)_4\text{PtCl}_4$  and  $(\text{TTF})_2\text{NiS}_4\text{C}_4\text{H}_4$  (TTF = tetrathiafulvalene) are described and used to illustrate the application of electrical property measurements:

## Introduction

The strong current interest in inorganic and organic compounds which display pseudo-one dimensional solid state properties has been noted in several other papers in this Symposium. This interest has been manifested in a rather large number of special symposia<sup>(1)</sup> and publications, particularly in the physics journals, in the last few years.

In many of these compounds the "one-dimensional" solid state properties derive from interactions between planar molecular units which are "stacked" together to form columns or even metal atom chains along one direction in the solid. The tendency of planar molecules to stack in columns can be understood simply from the standpoint of packing efficiency considerations although in certain cases specific bonding interactions have been evidenced by unusually short intermolecular separations.<sup>(2)</sup> In the case of planar transition metal complexes, the interactions among the metal and ligand  $\pi$ -orbitals which occur within these stacks can provide a continuous pathway for electron delocalization along one direction in the solid, detectable as anisotropic electrical conductivity. Such effectively one-dimensional solid state interactions can result in unique properties and property combinations. For example, in addition to pseudo-metallic conductivity and optical reflectivity behavior along the stacking direction and effectively insulating character perpendicular to this direction, evidence has been obtained for unusual structural distortions, analogous to Jahn Teller effects in molecular systems, which result in gradual metal to insulator transitions at low temperatures.<sup>(3)</sup> In certain cases these structural distortions are believed to give rise to

cooperative electron transport, via "charge density waves," which presumably enhance the conductivity at low temperatures above that which could be anticipated on the basis of ordinary one-electron scattering theory. (3, 4)

In addition to systems with one-dimensional metallic properties, there are a considerably larger number of planar metal complexes where stacking interactions in the solid state give rise to unusual properties, including highly anisotropic conductivity behavior, but where electronic or structural factors lead to thermally activated conductivities. (5) Work on such "one-dimensional semiconductors" constitutes an important area of study within the general topic of "solids with one-dimensional interactions" and has provided much useful information regarding structure-property relationships in these materials.

The primary objective of this paper is to illustrate, by means of specific examples chosen from our past and current research, how electrical property measurements can be of value in the study of the intermolecular orbital interactions in transition metal complex systems of this type and in deducing information regarding the solid state electronic structure. To facilitate this discussion a brief description of electrical conductivity and some other electrical properties has been included. For a more detailed account as well as a description of the various experimental techniques which are used to determine these properties, the reader is referred to any of several excellent books on the subject. (6)

## THE MEASUREMENT OF ELECTRICAL PROPERTIES

### Electrical Conductivity

The measurement of electrical conductivity is essentially the determination of the amount of charge transported per second across a unit area of

sample due to an applied unit electric field. Assuming the conductivity is primarily "electronic" in nature (as opposed to "ionic"), as seems to be the case for most transition metal complex solids, the charge carriers are either electrons or their positive counterparts, "holes" and the conductivity is determined by the number of such species and their velocity (mobility) in the applied field, i. e.,  $\sigma \propto n \mu$ , where  $\sigma$  is the conductivity,  $n$  is the number of carriers and  $\mu$ , their mobility in  $\text{cm}^2/\text{volt-sec}$ . The mobility, in very simple terms, reflects the facility with which the carrier can move through the sample and thus, in a crystal comprised of molecular units, provides a good measure of the intermolecular orbital interactions.

The reciprocal of the conductivity is the resistivity,  $\rho$ , which is the resistance per unit cube and is measured in ohm cm; the unit of conductivity is thus  $\text{ohm}^{-1} \text{cm}^{-1}$ . The conductivities of a number of representative materials at 25°C are compared in Figure 1 on a logarithmic scale of  $\text{ohm}^{-1} \text{cm}^{-1}$ . The terms "metal," "semiconductor," and "insulator" imply a certain level of conductivity, as is illustrated by the approximate ranges in Figure 1, but, moreover, refer to the manner in which the conductivity varies with temperature as well as other characteristic electrical, optical, and magnetic properties. For a metal the conductivity generally decreases with increasing temperature in the manner,  $\sigma \propto 1/T$ , whereas for semiconductors and insulators the conductivity generally increases, often exponentially, i. e.,  $\sigma \propto \exp(-\Delta E/kT)$ .

As is indicated in Figure 1, molecular solids, and indeed most organic and metal complex materials fall in this category, usually exhibit



rather low electrical conductivities ( $10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$ ) reflecting the rather weak Van der Waals interactions between the molecular units in the solid. There are a number of molecular solids with substantially higher conductivities, however, ranging up to  $\sim 800 \text{ ohm}^{-1} \text{ cm}^{-1}$  for tetraselenofulvalene • tetracyanoquinodimethane (TSeF • TCNQ).<sup>(7)</sup>

In this compound and several other structurally analogous organic and inorganic compounds the conductivity exhibits an inverse dependence on temperature over a limited temperature region and other characteristically "metal-like" properties are observed. Included in this group are polymeric sulfur nitride,  $(\text{SN})_x$ , and a group of partially oxidized, square planar platinum and iridium complexes, collectively referred to as "KCP" in Figure 1, both of which are discussed elsewhere in this Symposium.

With the exception of these relatively few materials, most transition metal complexes exhibit properties more typical of semiconductors with conductivities usually less than  $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$  and a thermally activated conductivity behavior. The thermal activation energy, which is derived from plots of  $\log \sigma$  vs  $1/T$ , in these cases, may result from either the production of charge carriers, as, for example, by direct band gap excitation in an intrinsic semiconductor, or from the carrier motion, as in systems where the conduction proceeds by a short range, thermally activated, hopping process.

In either case, extremely small amounts of impurities and crystalline defects can play an important role in determining both the magnitude of the conductivity and the activation energy. The elucidation of such effects is often a difficult task, requiring careful control of sample purity and form as well as experiments on samples in various stages of purification.

### Other Electrical Properties

A characteristic feature of many semiconductors and insulators is an increase in conductivity on absorption of light in a particular frequency range. This "photoconductivity" usually reflects an increase in the number of free carriers in the solid due to their photoexcitation from filled bands, donor levels or trapping states. The spectral response and quantum efficiency of the photoconductivity can be used to deduce information regarding the energy band structure of a semiconductor and the carrier lifetimes (or mobilities).

Another electrical property of fundamental importance is the thermoelectric power, or Seebeck effect. Its sign, magnitude and temperature dependence can provide information about the sign of the charge carriers and their mobility as well as the band structure of the solid. It is essentially the voltage generated between two junctions of a material when the two junctions are held at different temperatures and it is determined simply by measuring the induced voltage and dividing by the temperature difference. The sign of the thermopower is defined as the polarity of the cold junction and usually corresponds to the sign of the majority carrier (i. e. , positive for holes, negative for electrons). Its magnitude is characteristically small ( $< 100 \mu\text{V}/\text{degree}$ ) for metals and considerably larger ( $> 100 \mu\text{V}/\text{degree}$ ) for semiconductors. The temperature dependence is also usually larger for semiconductors where a relation of the type  $S = B/T + K$  (where  $S$  is the thermopower and  $B$  and  $K$  are constants) is often observed. Various theoretical expressions of this general form have been derived on the basis of band theory and used to relate the experimental data to such features of the conduction

process as the position of the Fermi level in relation to the band edges, the effective mass of the carriers, the electron/hole mobility ratio and the nature of the carrier scattering mechanism.

A variety of other types of electrical measurements<sup>have been</sup>/employed in the study of semiconductor materials. Hall Effect measurements have been used to determine the sign and concentration of charge carriers as well as, in conjunction with conductivity measurements, to deduce mobilities. The mobilities, which are quite sensitive to the intermolecular orbital overlaps in molecular solids, can also be determined directly, with less ambiguity, by injecting a pulse of charge carriers, using light or an electric field, and measuring their transit time over a known distance in a known field. Although such methods have proven quite useful in the study of many inorganic semiconductors they have not found wide application thus far in work on molecular solids due, perhaps in part, to difficulties in obtaining suitable single crystal samples of appropriate dimensions, as well as the somewhat higher degree of sophistication required for their meaningful application. For details regarding these and the various other electrical property measurement methods which are not discussed here, the previously mentioned reference sources<sup>(6)</sup> should be consulted.

#### THE APPLICATION OF ELECTRICAL MEASUREMENTS TO THE STUDY OF SOME METAL COMPLEX SYSTEMS

##### Magnus' Green Salt

The crystal structure of Magnus' Green Salt (MGS),<sup>(8)</sup>  $[\text{Pt}(\text{NH}_3)_4\text{PtCl}_4]$ , is illustrated in Figure 2. Of particular interest are the linear chains of Pt atoms which result from the columnar stacking of the constituent planar complex

units. The Pt-Pt separations within these chains ( $3.25\text{\AA}$ ) is substantially shorter than the separations between chains ( $6.39\text{\AA}$ ) suggesting the possibility of highly directional solid state interactions. The first evidence for the existence of such interactions was the green color of this compound which was not the expected consequence of the combination of the colorless  $\text{Pt}(\text{NH}_3)_4^{2+}$  and pink  $\text{PtCl}_4^{2-}$  ions. Spectral studies carried out over the past 25 years on MGS have led to the identification of the source of the green color as a "window" in the absorption spectrum at  $\sim 20,000\text{ cm}^{-1}$  arising from a red shift and intensification of the largely intramolecular " $d \rightarrow d$ " transitions on the  $\text{PtCl}_4^{2-}$  ion. <sup>(9)</sup>

In one of the earlier studies of this absorption spectrum an apparent broad, strong, absorption band was observed in the near infrared region in the vicinity of  $6000\text{ cm}^{-1}$  which was thought to be possibly intermolecular in origin. <sup>(10)</sup> This observation led to the postulation of an energy band description for the electronic structure of MGS which has been widely used in subsequent work on this and other "metal-chain" systems (Figure 3).

The extended interaction of the filled  $d_{z^2}$  and empty  $p_z$  orbitals on the platinum atoms in the linear chains is viewed here as giving rise to energy bands of appreciable width in the solid, much like the energy bands in covalent inorganic semiconductors, only highly directional in character. The "near infrared absorption band" was attributed to transitions across the "forbidden energy gap" between these bands, which then, presumably amounts to  $<1\text{ eV}$ .

The possibility that thermal or photoexcitation of electrons between these bands could lead to mobile charge carriers in either or both bands, and



consequently anisotropic semiconductivity or photoconductivity, was anticipated. Subsequent observations by Collman and co-workers<sup>(11)</sup> and by Gomm, Thomas, and Underhill<sup>(12)</sup> verified these predictions and, moreover, gave results which seemed to be in reasonable quantitative agreement with the intrinsic band model description in Figure 3. This agreement was short lived, however, as later spectral studies on single crystals of MGS<sup>(13)</sup> failed to substantiate the earlier claim of a strong absorption band in the near infrared, as would be anticipated from the presumed band gap of  $<1$  eV, and semi-quantitative band structure calculations<sup>(14)</sup> led to an estimate of 4.5 eV for the  $d_{z^2}-p_z$  band gap, which would be characteristic of a good insulator.

To answer the questions regarding the origin of the conductivity in MGS and the nature of the solid state electronic interactions raised by these observations, the growth of suitable single crystal samples of MGS and a detailed study of their electrical properties was undertaken. The subsequent development of a silica gel procedure<sup>(15)</sup> for the growth of MGS crystals permitted, for the first time, the preparation of large, high quality crystals of appreciable cross section. Rectangular parallelepiped crystals 1 - 2 mm long and up to 0.7 mm  $\times$  0.7 mm in cross-section were obtained in this manner and, after screening for defects by examination under a microscope and study of the crystal morphology by x-ray precession methods, were mounted for conductivity and thermoelectric power measurements. Conductivities were measured using the standard four-electrode, voltage probe method,<sup>(6)</sup> with two end contacts and two voltage probes attached along one direction in the crystal, and also by the Montgomery method<sup>(16)</sup> with four electrodes at four parallel edges of



the crystal, to determine the conductivity anisotropy. Contacts were made using Dupont silver paint #7941 and fine gold wire leads.

A typical  $\log \sigma$  vs  $1/T$  plot obtained in the voltage-probe studies is illustrated in Figure 4. The linearity of this plot over the wide temperature range studied (120° to 350°K) suggests that we are dealing with one thermally activated conduction process in this temperature regime.

Measurement of the conductivity anisotropy both by four-probe measurements on individual samples and by the Montgomery method<sup>(16, 17)</sup> gave values in the range 18→25/1 for the ratio of the  $\sigma_c$  (metal chain direction) and  $\sigma_a$  axis conductivities. This is somewhat less than the anisotropy exhibited by other one dimensional systems<sup>(3, 18)</sup> but is still basically consistent with the suggestion that the predominant solid state interactions in MGS are along the platinum chains.

A detailed study of the conductivity as a function of frequency was not carried out; however, preliminary two electrode A.C. measurements at room temperature on a single crystal sample indicated essentially no change from the D.C. conductivity value with A.C. frequencies up to at least 1000 hertz.<sup>(17)</sup> This observation is in agreement with expectations for band-type semiconductors where the carriers are relatively mobile in an applied field.

In addition to these conductivity studies, measurements of the thermopower were carried out on several crystals as a function of temperature using two small gold-Advance thermocouples attached to the ends of the crystal with silver paint.<sup>(17)</sup> The crystal and thermocouples were suspended from single crystal quartz blocks, one of which was electrically heated to provide the

required temperature gradient. In each case positive thermopower values were observed, suggesting that holes are the majority carriers. The large magnitude of the thermopower and its essentially linear dependence on  $1/T$  (Figure 5) is consistent with previous observations on semiconductors and with the expression,  $S = k/e [\Delta E/kT + A]$ , derived by Fritzsche for a semiconductor in which only one band is involved in the conduction process.<sup>(19)</sup> The  $\Delta E$  in this expression is basically the activation energy for charge carrier production and, in the case of a band type semiconductor is equivalent to the thermal activation energy for conductivity. The substantially higher value observed for the conductivity activation energy in this same crystal could arise, in part, from an activation energy associated with the charge carrier motion, as in a narrow band, hopping type semiconductor.

The results of the voltage-probe D.C. conductivity measurements on 19 different crystals of MGS obtained from 4 crystal growth preparations are summarized in Table I. These data reveal several interesting features regarding the conduction process in MGS. In particular, whereas the room temperature conductivities of crystals obtained from the same preparation are in reasonably good agreement, the variation from one preparation to the next is as much as three orders of magnitude. A marked variation in the thermal activation energy for conductivity is also apparent between preparations with, in general, a lower thermal activation energy for the samples of higher conductivity. Careful examination of these crystals under a microscope and by x-ray precession methods revealed no apparent structural or morphological differences among the samples from different preparations. Microanalytical

determinations indicated small amounts (ppm level) of other transition elements (primarily Fe, Cu, and Pd) but no obvious variations in composition from one preparation to the next.

TABLE I.

D. C. Conductivity Data for MGS Crystals<sup>a</sup>

<u>Preparation</u>	<u>Number of Samples</u>	<u>c-Axis Conductivity at 25°C (ohm<sup>-1</sup> cm<sup>-1</sup>)</u>	<u>Thermal Activation Energy (eV)</u>
A	6	$4.7(\pm 2.4) \times 10^{-5}$	0.352 ( $\pm 0.033$ )
B	3	$8.5(\pm 4.2) \times 10^{-4}$	0.257 ( $\pm 0.025$ )
C	4	$1.3(\pm 0.3) \times 10^{-3}$	0.255 ( $\pm 0.020$ )
D	6	$7.5(\pm 1.6) \times 10^{-3}$	0.212 ( $\pm 0.012$ )

<sup>a</sup>Average values with average deviations in parentheses.

By means of additional experiments carried out using the same  $\text{Pt}(\text{NH}_3)_4^{2+}$  and  $\text{PtCl}_4^{2-}$  solutions, it was shown that certain solutions consistently gave crystals of higher conductivity, suggesting that differences in the composition of these solutions were responsible for the observed conductivity variations. On the basis of these findings and the previously mentioned arguments against the intrinsic band model, it was suggested that the conductivity in MGS was impurity dominated. (13a, 20)

The first definitive information regarding the nature of these impurities was provided by EPR measurements on MGS carried out on both single crystal and powder samples prepared under different experimental conditions. (21) An axially symmetric resonance was observed in the single

crystal samples which was identified, on the basis of the  $g$ -values and the observed hyperfine pattern, as arising from an electron in a  $d_{z^2}$ -like state extending over several Pt atoms. Spectrophotometric analysis of the solutions used to prepare MGS and doping experiments suggested further that the source of these unpaired electrons were  $Pt^{IV}$  complexes present in the solutions. These  $Pt^{IV}$  complexes apparently induce a partial oxidation of the  $Pt^{II}$  ions in the solid which is compensated by the addition of negative ions (presumably halides), either at interstitial sites or as a replacement for the neutral  $NH_3$  groups. The presence of such halide ions, particularly at interstitial sites, could facilitate electron transfer between the platinum chains, thus accounting for the observation of the substantially lower (18-25X) but still significant conductivity perpendicular to the metal chain direction in MGS. The existence of  $Pt^{IV}$  species in the nominal  $Pt^{II}$  complexes used to prepare MGS was found to be a general occurrence, presumably due to air oxidation or to incomplete reduction of the  $Pt^{IV}$  starting material in the preparation of the  $Pt^{II}$  complexes.

EPR studies on some of the same crystals employed in the previously mentioned conductivity studies revealed a general correspondence between the intensity of the EPR resonance and the conductivity of the crystals, thus establishing a relationship between the impurity induced conductivity effects and the presence of " $Pt^{III}$ -like" states in the solid.

Using the available information regarding the nature of the "impurity" states in MGS and the results of the semiquantitative band structure calculations, a modified "band model" for the MGS electronic structure can be constructed



which appears to account for much of the available data. This model (Figure 6) is similar to the intrinsic band model proposed by Miller,<sup>(10)</sup> in that " $d_{z^2}$ " and " $p_z$ " bands of significant width are postulated; however, consistent with the theoretical calculations<sup>(14)</sup> and spectral observations<sup>(9, 13)</sup> here the  $d_{z^2}$ - $p_z$  band gap is on the order of 4.5 eV and acceptor levels, corresponding to the  $Pt^{III}$ -like states localized in the vicinity of the charge compensating defects, have been introduced close to the top of the  $d_{z^2}$  band.

Intrinsic MGS in this context would be a good insulator and the observed conductivity is attributed entirely to the presence of the "impurity" states. Thermal excitation of electrons from the  $d_{z^2}$  band into these acceptor levels should lead to hole conduction in the  $d_{z^2}$  bands, consistent with the observed "p-type" conductivity behavior. Also the essentially frequency independent conductivity as well as the weak character of the photoconductivity response observed by Collman<sup>(11)</sup> in the near infrared is understandable on this basis, as is the lack of any strong absorption bands in this region, considering the relatively low concentration of impurity states present [200 ppm " $Pt^{III}$ " sites estimated by EPR<sup>(21)</sup>]. It is also possible to account for the apparently smaller thermal activation energies observed for the crystals of higher conductivity by considering the likelihood of impurity banding in these presumably more highly doped samples.

Although this extrinsic band model can be used to account for much of the available information concerning the electrical properties of MGS, especially in view of the thermopower data obtained, the alternative possibility that conventional band theory is not appropriate to MGS and that a more



localized description of the electronic structure is required clearly cannot be discounted at this point. A definite answer to this question must await further studies on this system, including a direct determination of the charge carrier mobility.

(TTF)<sub>2</sub>NiS<sub>4</sub>C<sub>4</sub>H<sub>4</sub>

Bis(tetrathiafulvalene)-bis(1, 2-ethylenedithiolene)nickel [(TTF)<sub>2</sub>NiS<sub>4</sub>C<sub>4</sub>H<sub>4</sub>] is a member of a new series of  $\pi$ -donor-acceptor compounds prepared by the interaction of tetrathiafulvalene (TTF) with neutral bis-dithiolene metal complexes. <sup>(22)</sup> It crystallizes from acetonitrile solution as large (~2 mm on a side) single crystals suitable for detailed conductivity measurements. The results of such measurements, when examined in the light of the other solid state properties and information obtained from a complete three-dimensional crystal structure determination, suggest specific interactions of a quite directional character among the constituent planar molecular units in the solid and thus provide a good illustration of the utility of electrical conductivity as a tool for investigating solid state interactions.

In addition to the conductivity studies, electronic absorption spectral, magnetic susceptibility and esr measurements were carried out on this compound. <sup>(22a)</sup> The results indicated that charge transfer between the neutral diamagnetic TTF and NiS<sub>4</sub>C<sub>4</sub>H<sub>4</sub> units had occurred in the solid state to give paramagnetic NiS<sub>4</sub>C<sub>4</sub>H<sub>4</sub><sup>-</sup> ions. These were identified by both their characteristic absorption spectrum and by their anisotropic g-values. The magnetic measurements indicated essentially Curie type paramagnetism but with a Curie constant appropriate for only one unpaired electron per

(TTF)<sub>2</sub>NiS<sub>4</sub>C<sub>4</sub>H<sub>4</sub> formula unit. This was identified as the electron on the NiS<sub>4</sub>C<sub>4</sub>H<sub>4</sub><sup>-</sup> ions on the basis of the esr and spectral results. The fate of the electron left on the TTF<sup>+</sup> units after charge transfer is suggested by the results of the structural investigation.<sup>(22b)</sup> This compound crystallizes in the monoclinic space group C2/m with  $a = 25.80\text{\AA}$ ,  $b = 10.67\text{\AA}$ ,  $c = 9.99\text{\AA}$  and  $\beta = 119.67^\circ$ .

Views normal to the (010) and (100) planes are shown in Figures 7 and 8, respectively. The structure consists of four (TTF)<sub>2</sub>NiS<sub>4</sub>C<sub>4</sub>H<sub>4</sub> formula unit cell molecules per / with the TTF and NiS<sub>4</sub>C<sub>4</sub>H<sub>4</sub> / arranged in alternate strips parallel to the (100) plane. The NiS<sub>4</sub>C<sub>4</sub>H<sub>4</sub> units are oriented with their molecular planes parallel to the (100) plane and are located at  $y = 0$  and  $1/2$ , well separated from one another and the other molecules in the unit cell. Three structurally distinct TTF molecules occur, labeled I, II, and III in the figures.

The molecules I and II form a columnar stack along [010] with the two units at II and II' in Figure 8 rotated by  $60^\circ$  with respect to those at I and in a fully eclipsed configuration. These two units (II and II') are separated by  $3.48\text{\AA}$ , suggesting a significant bonding interaction. These are identified as the TTF<sup>+</sup> ions in the structure which are presumably held together in an eclipsed configuration by means of interaction of the half filled  $b_{1u}$  orbitals<sup>(23)</sup> on the two units. The electrons left after charge transfer are thus presumably paired up in the resultant bonding molecular orbital. These (TTF<sup>+</sup>)<sub>2</sub> dimer units are effectively connected to one another in two dimensional sheets parallel to the (100) plane by means of the neutral TTF molecules at I and III. Those

at I are separated by  $3.60\text{\AA}$  from the  $(\text{TTF}^+)_2$  pairs and could potentially interact through overlap of the  $b_{1u}$   $\pi$ -orbitals on each unit. The ones at III also make close sulfur-sulfur contacts to the  $\text{TTF}^+$  units in the dimer ( $3.51\text{\AA}$ ) thus bridging these dimers together along the  $[001]$  direction (Figure 9). In this case the interaction, if indeed one occurs, must involve the  $\pi$ -orbitals of the III unit and the  $\sigma$ -orbitals of the  $(\text{TTF}^+)_2$  dimer.

Using single crystal samples cut into rectangular parallelepipeds of  $\sim 1.0\text{ mm} \times 0.7\text{ mm} \times 0.4\text{ mm}$  dimensions, conductivity measurements were carried out by means of the Montgomery method,<sup>(16)</sup> with contacts placed at four parallel edges of the samples. Single crystal x-ray precession measurements were used to determine the relationship to the principal crystallographic directions. In this manner the conductivities along the  $[010]$  and  $[001]$  direction and an approximate value for the conductivity perpendicular to the  $(100)$  plane were determined as a function of temperature. A thermally activated conductivity behavior much like that in MGS was observed with a thermal activation energy of  $0.23 \pm 0.02\text{ eV}$  which was approximately independent of direction. The conductivity, however, showed a strong direction dependence and was found to be highest along the  $[010]$  or TTF stacking direction in the solid. The value observed here ( $7.4 \times 10^{-3}\text{ ohm}^{-1}\text{ cm}^{-1}$ ) is relatively high on the scale of molecular semiconductors and indicates an appreciable  $\pi$ -orbital interaction among the TTF units in the stack. The conductivity along the  $[001]$  axis, although definitely lower than that along  $[010]$ , is also appreciable suggesting that the TTF  $\sigma$ - $\pi$  orbital interactions in this direction also provide a pathway for electron delocalization in the solid.

The lowest conductivity value determined ( $\sim 5.0 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ ) is that perpendicular to the (100) plane, through the  $\text{NiS}_2\text{C}_4\text{H}_4^-$  units, where the interatomic separations are relatively large and the orbital interactions are weakest.

The origin of the conductivity in this compound is not yet known with certainty, although it is tempting to speculate that the electron pair presumably involved in the  $(\text{TTF}^+)_2$  binding can be thermally activated into conduction band states to produce carriers. Alternative mechanisms, perhaps even involving impurity species, certainly cannot be discounted at this point, especially in view of the results obtained with MGS. Further investigations of this unusual material are currently in progress.

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### Figures

- Figure 1. Approximate conductivity scale for some representative solid state materials.
- Figure 2. The crystal structure of Magnus' Green Salt.
- Figure 3. Energy band model for MGS [Adapted from J.R. Miller, J. Chem. Soc. 713 (1965)].
- Figure 4. Representative  $\log \rho$  vs  $1/T$  plot for a MGS crystal wired for D.C. voltage probe measurements along the  $c$  axis.
- Figure 5. The thermopower of MGS as a function of  $1/T$ . The slope of the  $\log \rho$  vs  $1/T$  curve for this same crystal is included for purposes of comparison.
- Figure 6. Extrinsic band model description for the electronic structure of MGS. The acceptor levels correspond to localized " $\text{Pt}^{\text{III}}$ -like" states, each containing one unpaired electron.
- Figure 7. The unit cell of the  $(\text{TTF})_2\text{NiS}_4\text{C}_4\text{H}_4$  crystal structure viewed down  $[010]$ . The molecules whose centers are at  $y = 1/2$  are darkened; except for molecules labeled II, all other molecules have their centers at  $y = 0$ . The three types of TTF units discussed in the text are identified by Roman numerals.
- Figure 8. A view of the  $(\text{TTF})_2\text{NiS}_4\text{C}_4\text{H}_4$  structure normal to  $(100)$  showing the three types of TTF molecules (labeled I, II, and III).
- Figure 9. Interaction of TTF units in  $(\text{TTF})_2\text{NiS}_4\text{C}_4\text{H}_4$ .

THE SYNTHESIS AND ELECTRICAL PROPERTIES OF METAL MERCAPTIDES  
OF 1,4-DIMERCAPTOBENZENE

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Special Report to Mr. M. Broadhurst  
National Bureau of Standards, Washington D.C.

THE SYNTHESIS AND ELECTRICAL PROPERTIES OF TRANSITION METAL MERCAPTIDES  
OF 1,4-DIMERCAPTOBENZENE<sup>1</sup>

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## ABSTRACT:

The synthesis of a number of new transition metal mercaptides of the ligand 1,4-dimercaptobenzene is reported. Several of these mercaptides, which are regarded as S-bridged polymers, behave like semiconductors within the temperature range investigated. An interesting result of the study is the relatively low electrical resistivity ( $\rho = 40 \text{ ohm}\cdot\text{cm}$  at  $25^\circ\text{C}$ ) of the Cu(I) complex of composition  $[\text{Cu-S-C}_6\text{H}_4\text{-S-Cu}]_n$ . Copper thiophenolate,  $[\text{C}_6\text{H}_5\text{SCu}]_n$  is also found to behave like a semiconductor, with an electrical resistivity of  $5.1 \times 10^4 \text{ ohm}\cdot\text{cm}$  at  $25^\circ\text{C}$ . The reaction of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) with Cu(I) complexes cleaves the Cu-S bonds and leads to the formation of the Cu(I) salt of the TCNQ radical anion,  $\text{Cu}^+\text{TCNQ}^{\cdot-}$ .

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## INTRODUCTION:

Extensive studies of the coordination chemistry of unsaturated or aromatic 1,2-dithiol ligands have been reported<sup>2-5</sup>, and semiconductor behavior has been noted for transition metal complexes of  $\alpha$ -dithiodiketones, dithiooxamide (rubeanic acid) and N-substituted dithiocarbamates.<sup>6-8</sup> However, no information is available concerning 1,4-dimercaptobenzene and other aromatic polythiols as potential ligands. We became interested in these ligands and their coordination polymers with the object of finding new thermally stable materials having semiconducting properties. The ligands chosen meet the requirements to form complexes with these properties. First, they are thermally stable and possess donor atoms separated by an aromatic ring. Secondly, each ligand can bind two metal atoms, and substantial back-coordination of the metal d electrons to the ligand-based antibonding orbitals as well as the formation of sulfur-bridged metal chains could facilitate electron transport. In this paper, we report the synthesis and the chemical and electrical properties of a number of new polymeric mercaptides of 1,4-dimercaptobenzene having the general formulae  $[\text{M-S-C}_6\text{H}_4\text{-S-M}]_n$  ( $\text{M}=\text{Cu(I)}$  and  $\text{Ag(I)}$ ) and  $[\text{M-S-C}_6\text{H}_4\text{-S-}]_n$  ( $\text{M}=\text{Cu(II)}$ ,  $\text{Hg(II)}$ ,  $\text{Pb(II)}$ , and  $\text{Ni(II)}$ ). For comparison, the properties of copper thiophenolate are also given.



## EXPERIMENTAL:

Physical Measurements. The infrared spectra of the complexes were obtained from KBr pellets, using a Beckman Model IR-33 for the 4000-600  $\text{cm}^{-1}$  range and Perkin-Elmer Models 180 and 457 for the 600-300  $\text{cm}^{-1}$  range. X-Ray powder patterns were obtained on a G.E. XRD-6 diffractometer with Cu  $K_{\alpha}$  radiation and a crystal monochromator to eliminate the Cu  $K_{\beta}$  line. The X-ray tube voltage was 45 kv; the amperage 15 ma; the entrance slit  $1.0^{\circ}$  medium resolution and the exit slit  $0.2^{\circ}$ . The proton magnetic resonance spectra were recorded on a TR-60 spectrometer. Solid state absorption spectra of complexes wherever possible were obtained on KBr pellets using a Beckman Model DK-2A spectrophotometer.

Synthesis of 1,4-Dimercaptobenzene. The ligand 1,4-dimercaptobenzene was prepared via the reductive cleavage of 1,4-bis(ethylthio)benzene according to the method of Adams and Ferretti.<sup>9</sup> A solution of *p*-dibromobenzene in 2,4-lutidine was treated with the sodium salt of ethyl mercaptan and catalytic amounts of cuprous bromide to form the thioether.<sup>10</sup> The thioether was subsequently cleaved by sodium in liquid ammonia. The sodium salt of 1,4-dimercaptobenzene was isolated after evaporation of liquid ammonia. The free dithiol was obtained by treatment of the aqueous solution of the sodium salt with hydrochloric acid. The ligand was further purified by vacuum sublimation before use, mp  $97.5-98.5^{\circ}\text{C}$ .

Preparation of Metal Complexes. In general the metal complexes were prepared by mixing under argon hot solutions of the appropriate metal compound (cupric chloride, cuprous chloride, mercuric chloride, silver acetate, lead acetate, and nickel tetracarbonyl) and dithiol in stoichiometric amounts. Argon was

Table I

## ELEMENTAL ANALYSES AND PHYSICAL PROPERTIES OF THE TRANSITION METAL MERCAPTIDES

Entry	Complex	Solvent	Color	C	H	Analyses <sup>a</sup> S	Metal	Dec. Temp. (°C)
1	[Cu-S-C <sub>6</sub> H <sub>4</sub> -S-] <sub>n</sub>	H <sub>2</sub> O	Yellow-brown	35.42 (35.39)	2.06 1.96	31.56 31.46	31.01 31.18)	>250
2	Cu-[S-C <sub>6</sub> H <sub>4</sub> -S-Cu] <sub>3</sub> <sup>*</sup>	H <sub>2</sub> O-NaOH-Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	Yellow	32.21 (32.04)	1.88 1.78	28.78 28.51	37.70 37.67	>270
3	[Cu-S-C <sub>6</sub> H <sub>4</sub> -S-Cu] <sub>n</sub>	2,4-lutidine	Yellow	27.23 (26.96)	1.52 1.50	23.93 23.99	47.74 47.55)	>330
4	[Cu-S-C <sub>6</sub> H <sub>4</sub> -S-Cu] <sub>n</sub>	Solid state	Yellow	27.99 (26.96)	1.58 1.50	26.06 23.99	46.04 47.55)	>330
5	[Ag-S-C <sub>6</sub> H <sub>4</sub> -S-Ag] <sub>n</sub>	2,4-lutidine	Yellow	20.45 (20.25)	1.01 1.12	17.85 18.02	60.51 60.61)	N
6	[Hg-S-C <sub>6</sub> H <sub>4</sub> -S-] <sub>n</sub>	2,4-lutidine	Yellow	21.30 (21.15)	1.19 1.17	18.72 18.82	58.84 58.86)	285-90 <sup>b</sup>
7	[Pb-S-C <sub>6</sub> H <sub>4</sub> -S-] <sub>n</sub>	H <sub>2</sub> O-CH <sub>3</sub> OH	Brown	21.01 (20.74)	0.79 1.15	18.45 18.45	59.58 59.65)	>320
8	[C <sub>6</sub> H <sub>5</sub> SCu] <sub>n</sub>	C <sub>2</sub> H <sub>5</sub> OH	Pale yellow	41.62 (41.73)	2.92 2.89	18.85 18.56	36.88 36.80)	>280
9	[Ni-S-C <sub>6</sub> H <sub>4</sub> -S-] <sub>n</sub>	THF	Black	36.60 (36.23)	2.24 2.01	32.56 32.24	28.49 29.52)	>310

<sup>a</sup> Calculated numbers in parentheses.<sup>b</sup> Melts with decomposition.

N No decomposition up to 350°C.

<sup>\*</sup> Complex in entry 2 appears to be a 1:2 mixture of [Cu-S-C<sub>6</sub>H<sub>4</sub>-S-Cu]<sub>n</sub> (shown by the x-ray powder diffraction) and [Cu-S-C<sub>6</sub>H<sub>4</sub>-S-]<sub>n</sub>, respectively.

used to prevent the oxidation of dithiol in air. The complexes were filtered, washed successively with ethanol and ether, and dried in vacuo at 150-200°C. The Cu(I) complex was also synthesized by heating an intimate mixture of freshly prepared cuprous chloride with excess dithiol under argon in the temperature range of 120-200°C. The excess ligand was removed by vacuum sublimation at 200°C. Copper thiophenolate was prepared by refluxing freshly prepared cuprous chloride and thiophenol in ethanol under a blanket of argon. The pale-yellow solid was filtered, washed with boiling ethanol and benzene. The solid was dried in vacuo at 150°C. The analytical data, colors, decomposition temperatures and solvents used are given in Table 1.

Reactions of 7,7,8,8-Tetracyano-p-quinodimethane (TCNQ) with Cu(I) Complexes of Thiophenol and 1,4-Dimercaptobenzene.

In a typical reaction, a powdered mixture of  $[\text{CuSC}_6\text{H}_5]_n$  and TCNQ in 1:1.5 mole ratio was charged into a Pyrex test tube and heated to 100°C in an oil bath under a blanket of argon. After four hours, the white crystals which deposited on the colder parts of the test tube were carefully removed and identified as diphenyl disulfide,  $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$ , mp 60-61°C. The melting point reported for diphenyl disulfide is 61-62°C.<sup>11</sup> The blue reaction mixture was then freed of unreacted TCNQ by vacuum-subliming the latter at 180-200°C. The X-ray powder diffraction pattern of the blue-black solid left in the sublimation pot was in agreement with that of  $\text{Cu}^+\text{TCNQ}^-$  prepared by the method of Melby, et al. The interplanar spacings (d values in Å) were: 7.96, 5.64, 5.04, 3.97, 3.53, 3.11 for  $\text{Cu}^+\text{TCNQ}^-$  obtained in this study, and 7.96, 5.65, 5.05, 3.98, 3.53, 3.12 for  $\text{Cu}^+\text{TCNQ}^-$  prepared by Melby, et al., method.<sup>12</sup> Similar reactions occurred when  $[\text{CuSC}_6\text{H}_5]_n$  and TCNQ were suspended in benzene at room temperature or heated in sealed Pyrex tubes above 45°C for several hours.

The Cu(I) complex of 1,4-dimercaptobenzene was similarly reacted with TCNQ in a sealed Pyrex tube in the temperature range of 120-160°C. The X-ray powder diffraction pattern of the reaction mixture revealed the presence of  $\text{Cu}^+\text{TCNQ}^-$ . It is reasonable to postulate that the other product was the polymeric sulfide,  $-(\text{S}-\text{C}_6\text{H}_4-\text{S})_n$ , which is known to be amorphous.<sup>13</sup> No further attempt was made to characterize the polymeric sulfide as it could not be separated from the reaction mixture.

Reactions of Metal Complexes with Organic Halides. A typical reaction was carried out by refluxing a sample of the mercaptide complex with excess organic halide (allyl bromide for the silver complex and methyl iodide for all other complexes) overnight. The insoluble solid residue in each case was filtered, washed with chloroform and dried in air. The X-ray powder diffraction pattern of the residue showed that it was either AgBr or CuI depending whether the silver complex or the copper complexes were reacted. The insoluble solid residue obtained from the reaction of Hg(II) complex with methyl iodide was purified twice from a N,N-dimethylformamide-methanol mixture. The very light yellow solid after drying melted at 145-145.5°C. The proton chemical shifts (in deuterated dimethylsulfoxide,  $\tau$  relative to  $(\text{CH}_3)_4\text{Si}$ ) were: 2.32 (quartet due to aromatic protons,  $J = 20$  cps) and 7.10 (doublet due to methyl protons,  $J = 17$  cps) in the area ratio of 9:30, consistent with the dimethylsulfonium iodide salt of 1,4-bis(methylthio)benzene,  $\text{I}(\text{CH}_3)_2\text{S}-\text{C}_6\text{H}_4-\text{S}(\text{CH}_3)_2\text{I}$ . The residue obtained after evaporation of N,N-dimethylformamide and drying was shown to be  $\text{HgI}_2$  by its X-ray powder diffraction pattern.

The filtrate after evaporation of the organic halide yielded a white solid when methyl iodide was used and an oil when allyl bromide was used to cleave the mercaptide complexes. The white solid after recrystallization from petroleum ether melted at 79-80°C. The reported melting point for 1,4-bis(methylthio)benzene is 84-85°C.<sup>14</sup> The proton chemical shifts (in CDCl<sub>3</sub>,  $\tau$  relative to (CH<sub>3</sub>)<sub>4</sub>Si) were: 2.87 due to aromatic protons and 7.55 due to methyl protons. The area ratio of 1:1.54 is consistent with 1,4-bis(methylthio)benzene, H<sub>3</sub>C-S-C<sub>6</sub>H<sub>4</sub>-S-CH<sub>3</sub>. The oily residue obtained from the reaction of silver complex with allyl bromide was identified as 1,4-bis(allylthio)benzene, H<sub>2</sub>C=CH-CH<sub>2</sub>-S-C<sub>6</sub>H<sub>4</sub>-S-CH<sub>2</sub>-CH=CH<sub>2</sub>. The proton chemical shifts (in CDCl<sub>3</sub>,  $\tau$  relative to (CH<sub>3</sub>)<sub>4</sub>Si) were: 2.87(aromatic), 6.55 (doublet, -CH<sub>2</sub>-), 4.18(multiplet, =CH-), 4.90(doublet, =CH<sub>2</sub>- trans to =CH-), and 5.12 (=CH<sub>2</sub>- cis to =CH-). The area ratios C<sub>6</sub>H<sub>4</sub>/-CH<sub>2</sub>-/-CH=/=CH<sub>2</sub> were 1/1/0.6/1, consistent with 1,4-bis(allylthio)benzene.

Resistivity Measurements. Two-probe measurement of d.c. resistivities were made on compressed powder compacts pressed at 97,000 psi, employing brass electrodes in conjunction with a Keithley Model 600A Electrometer for current measurements and a Keithley Model 160 Digital Multimeter for measurement of the voltage drop across the sample. D.C. resistivities were taken as averages before and after reversing the applied potential (usually 1.5 volts with a dry cell) to eliminate polarization effects. The electrical contact with the electrodes was made by G.E. Electronics Silver Print. The pellets were mounted between the electrodes and clamped in a small brass press described elsewhere.<sup>15</sup> The electrodes and the end plates of the brass press



were insulated with ceramic material. The cell was suspended in a Pyrex vessel from a Teflon rod. The leads were brought out through individual tungsten Pyrex seals, and the electrical connections to external circuit were arranged through these seals. The conductivity vessel was placed in a Dewar flask which served to keep the temperature constant. The cell was heated by an electrical tape wound around the Pyrex vessel. Temperatures in the vicinity of the sample were monitored by a chromel-alumel thermocouple attached to a potentiometer. Measurements were carried out in vacuo ( $10^{-4}$  torr) and argon atmosphere. Pellets were heated under vacuum to ca.  $80^{\circ}\text{C}$  for 2-3 hours to remove any moisture or volatile matter occluded during pellet pressing and cooled to room temperature before measurements were made. The near linear relationship between the applied voltage (12-50 volts for Ag(I) and Cu(II) complexes and 1.5-6 volts for Cu(I) complexes of thiophenol and 1,4-dimercaptobenzene) and the measured current indicates that the electrodes provided ohmic contact. No noticeable electrolysis was observed after prolonged passage of current, suggesting that the conductivity was electronic.

#### RESULTS:

Infrared Spectra. The infrared spectral data are given in Table 2. The spectra of all complexes are similar and characterized by the occurrence of a single absorption near  $810\text{ cm}^{-1}$  due to out-of-plane CH deformations of the aromatic ring, two absorptions near  $1380$  and  $1460\text{ cm}^{-1}$  assigned to C=C skeletal in-plane vibrations, and two absorptions near  $1010$  and  $1090\text{ cm}^{-1}$  attributed to C=S stretching vibrations.<sup>16</sup> A comparison with the spectrum of the

free ligand revealed that these principal absorption bands in the spectra of the complexes are also the common features of the ligand. There was no evidence of a S-H vibration in the spectra of the complexes which for the free ligand is located at  $2560\text{ cm}^{-1}$ . A slight shift to lower frequency of the principal absorption bands relative to the ligand was observed as a result of coordination of the metal to the ligand. A similar observation that the frequency of the strong dithiene bands does not change much with the metal was made previously by Schrauzer.<sup>3a</sup> Weak to strong-absorptions were found in the spectra of Cu(I) and Hg(II) complexes in regions where M-S stretching bands are generally observed and are so assigned.<sup>17</sup> The remaining absorptions in the region  $490\text{-}540\text{ cm}^{-1}$  are not readily assigned but are a common feature of all complexes. A band near  $1580\text{ cm}^{-1}$  of weak to medium intensity, not found in the ligand spectrum, can be readily assigned to a conjugated aromatic ring.<sup>16</sup>

X-Ray Diffraction Data. According to X-ray powder diffraction, all M(I) ions form crystalline complexes. All M(II) complexes reported here are amorphous with the exception of the Hg(II) complex, which is crystalline. It is interesting that the X-ray powder diffraction pattern of any one complex regardless of the method of preparation remains unchanged with no significant variations in the lattice parameters. It is, therefore, possible that the crystalline mercaptide complexes prepared in this study are not linear high polymers, but are small discrete, possibly cyclic, molecules. A final solution to the structures of these mercaptides should await single-crystal X-ray structural determination. Thus far, we have been unable to prepare single crystals. The X-ray powder data for the Cu(I) mercaptides are given in Table 3. As shown in the table, the data can be indexed based on a simple cubic unit cell. The density measurements indicate that there are four molecules in the unit cell of  $[\text{Cu-S-C}_6\text{H}_4\text{-S-Cu}]_n$  and eight for  $[\text{C}_6\text{H}_5\text{SCu}]_n$ .

Table 2

INFRARED SPECTRAL DATA OF THE MERCAPTIDES,  $\text{CM}^{-1}$ 


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$\text{HS-C}_6\text{H}_4\text{-SH}$	2560(m), 1900(w), 1640(w), 1480(ms), 1400(ms), 1260(m), 1120(vs), 1020(s), 900(ms), 810(vs).
$(\text{Cu-S-C}_6\text{H}_4\text{-S-Cu})_n$	1885(vw), 1625(w), 1560(m), 1470(vs), 1430(w), 1380(s), 1250(vw), 1175(vw), 1110(sh), 1092(vs), 1010(vs), 950(vw), 808(s), 535(m), 500(ms), 330(b,m).
$(\text{Cu-S-C}_6\text{H}_4\text{-S-})_n$	1620(bw), 1570(bw), 1390(m), 1190(vw), 1110(s), 1015(s), 810(s), 495(vs), 535(sh).
$(\text{Cu-S-C}_6\text{H}_5)_n$	3060(m), 1920(bw), 1890(vw), 1860(w), 1800(bvw), 1620(w), 1590(vs), 1485(vs), 1450(m), 1380(vw), 1330(vw), 1310(w), 1270(w), 1190(vw), 1090(s), 1030(s), 1005(vw), 740(vs).
$(\text{Pb-S-C}_6\text{H}_4\text{-S-})_n$	1480(vs), 1390(vs), 1260(vw), 1105(vs), 1015(s), 815(s).
$(\text{Ag-S-C}_6\text{H}_4\text{-S-Ag})_n$	1630(vw), 1475(vs), 1390(vs), 1350(vw), 1100(vs), 1010(s), 810(ms), 540(vs), 500(vs), 490(s).
$(\text{Hg-S-C}_6\text{H}_4\text{-S-})_n$	1930(vw), 1620(bw), 1580(vw), 1485(vs), 1400(s), 1110(vs), 1020(s), 830(ms), 540(s), 500(vs), 350(vs).
$(\text{Ni-S-C}_6\text{H}_4\text{-S-})_n$	1900(bw), 1620-70(b), 1570(m), 1475(vs), 1390(s), 1210(vw), 1180(w), 1090(b,m), 1015(m), 900(w), 810(m).

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b = broad

v = very

s = strong

m = medium

w = weak

sh = shoulder

Table 3

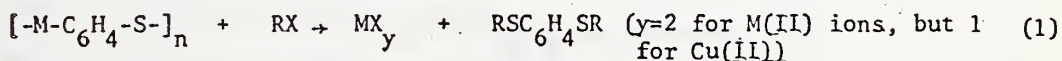
X-RAY DATA FOR THE COPPER(I) COMPLEXES OF 1,4-DIMERCAPTOBENZENE AND THIOPHENOL

Complex	hkl	I <sup>**</sup> <sub>obs.</sub>	d <sub>obs.</sub> (Å)	d <sub>calc.</sub> (Å)
[Cu-S-C <sub>6</sub> H <sub>4</sub> -S-Cu] <sub>n</sub>	100	80	10.53	10.49
	110	7	7.40	7.42
	200	7	5.24	5.24
	220	7	3.73	3.71
	300,221	5	3.48	3.50
	310	4	3.30	3.32
	311	3	3.18	3.16
	400	4	2.61	2.62
	410,322	4	2.54	2.54
[C <sub>6</sub> H <sub>5</sub> SCu] <sub>n</sub>	100	»100	12.31	12.20
	110	41	8.69	8.63
	210	26	5.44	5.55
	320	3	3.39	3.38
	420	4	2.73	2.73

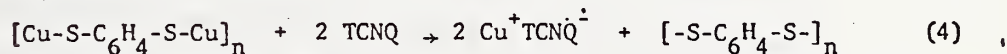
\* The calculated d spacings are based on a cubic unit cell with lattice constant  $a = 10.49 \text{ Å}$  for [Cu-S-C<sub>6</sub>H<sub>4</sub>-S-Cu]<sub>n</sub> and  $12.20 \text{ Å}$  for [C<sub>6</sub>H<sub>5</sub>SCu]<sub>n</sub>.

\*\* The observed intensities (I<sub>obs.</sub>) are peak heights of the diffraction lines on a diffractometer tracing.

Physical Properties and Chemical Reactivity of the Metal Complexes. Good thermal stability and resistance to acids and bases marked each of the complexes prepared in this study. However, with the exception of the silver complex, concentrated nitric acid reacted vigorously with most mercaptide complexes. A common feature of all the complexes is their insolubility in common organic and inorganic solvents. This often is a consequence of the tendency of coordinated thiol atoms to form bridges to adjacent metal atoms. All these properties suggest that the mercaptide complexes reported here should be coordination polymers involving sulfur bridges. Unfortunately, we were unable to determine the molecular weights because of the insoluble nature of these complexes. Contrary to previous experience with the reactions of S-bridged compounds, we found that several of these mercaptides were readily cleaved by organic halides under relatively mild conditions in accordance with reactions (1) and (2):



Furthermore, the Cu-S bonds were easily cleaved according to reactions (3) and (4) when we attempted to incorporate 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) in the polymeric structure of Cu(I) complexes hoping to increase their electrical conductivity via the formation of charge transfer complexes.



These reactions suggest that the formation of the charge transfer complex precedes the breaking of Cu-S bonds. In one experiment, the green reaction product obtained on heating TCNQ and copper thiophenolate at 45°C in a sealed Pyrex tube contained neither diphenyl disulfide nor  $Cu^+TCNQ^{\cdot -}$ . When



exposed to air, it began to smell strongly of thiophenol. Presumably, the formation of the charge transfer complex causes weakening of the Cu-S bond, which is then cleaved hydrolytically to form thiophenol or, in the absence of moisture, thermally to give diphenyl disulfide. This high reactivity of the mercaptide complexes towards electrophilic reagents such as organic halides and TCNQ indicates that the coordinated thiol atoms still retain much of their nucleophilic character. The complexes of Cu(I), Cu(II), Pb(II), and Ni(II) appeared to catalyze the decomposition of hydrogen peroxide, but only the Cu(II) complex showed some catalytic activity in the decomposition of hydrazine.

Electrical Properties. The variation of the resistivity with temperature is displayed in Fig. 3. Table 4 shows values for  $\rho_0$  (infinite temperature limit of the resistivity),  $E_a$  (thermal activation energy for conduction), together with the resistivity at 25°C. The results show a linear  $\log \rho$  vs.  $10^3/T$  relationship, consistent with a resistivity vs. temperature relationship of the form  $\rho = \rho_0 e^{E_a/kT}$  for the activated conductivity, where  $E_a$  is the thermal activation energy for conduction. The activation energies determined from the slopes of the straight line plots fall between 0.054 and 0.23 ev in the narrow temperature range of ca. 25-100°C available to us. There is good consistency between the measurements made on samples from the same batch in all cases. For example, repeat measurements on analytically pure copper thiophenolate (entry 8 in Table 1) and  $(\text{Cu-S-C}_6\text{H}_4\text{-S-Cu})_n$  (entry 3 in Table 1) reproduced to within  $\pm 5$  percent. The results, however, differed for samples of  $(\text{Cu-S-C}_6\text{H}_4\text{-S-Cu})_n$  prepared by different methods. Thus, the sample prepared

by a solid state reaction (entry 4 in Table 1) had a resistivity of 170 ohm·cm at room temperature as compared to 40 ohm·cm for the analytically pure sample prepared in 2,4-lutidine (entry 3 in Table 1). As the analytical data suggest, the higher resistivity in the former case is due to foreign impurities, possibly the polymeric sulfide,  $[-S-C_6H_4-S-]_n$ . As shown in Fig. 3, the  $\log \rho$  vs.  $10^3/T$  straight line plots for both samples are parallel and the thermal activation energy calculated from the observed slope is 0.054 eV in each case. This suggests that the conductivity is intrinsic to  $[Cu-S-C_6H_4-S-Cu]_n$ , and the higher resistivities of the impure samples are a result of the reduced mobilities of the charge carriers caused by the foreign impurity. For the most part the electrical resistivities of the M(II) complexes, including the Ag(I) complex, are very high and close to the range ascribed to insulators. Their resistivities are approximately of the same order of magnitude ( $\sim 10^9$  ohm·cm) and seem to correlate with the intensity of the band near  $1580\text{ cm}^{-1}$  in the infrared spectra, indicative of a conjugated aromatic ring and some degree of electron delocalization. The intensity of the  $1580\text{ cm}^{-1}$  band is weakest for the Hg(II) complex, which also has the highest resistivity.

Table 4

## ELECTRICAL RESISTIVITIES OF THE MERCAPTIDES

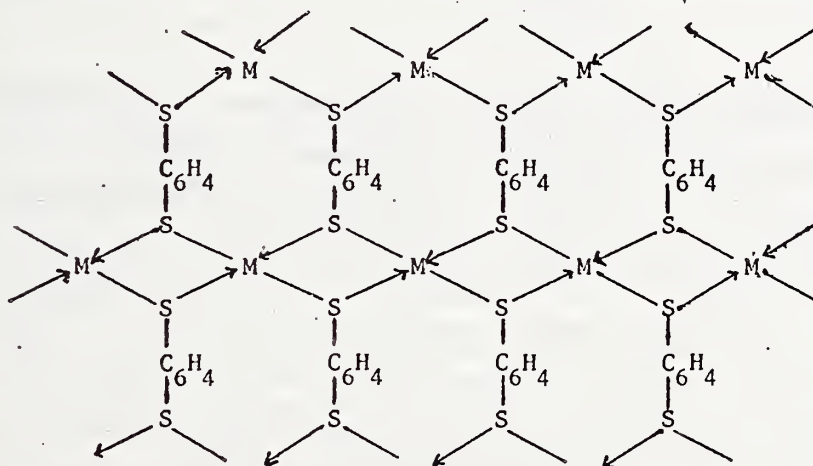
Entry	Complex	$\rho_{25}$ (ohm·cm)	$\rho_0$ (ohm·cm)	$E_a^*$ (ev)
1	$[\text{Cu-S-C}_6\text{H}_4\text{-S-Cu}]_n^{**}$	$4.0 \times 10^1$	0.32	0.054
2	$[\text{Cu-S-C}_6\text{H}_4\text{-S-Cu}]_n^{**}$	$1.7 \times 10^2$	1.33	0.054
3	$[\text{Cu-S-C}_6\text{H}_4\text{-S-}]_n$	$3.6 \times 10^8$	219	0.16
4	$[\text{C}_6\text{H}_5\text{SCu}]_n^{**}$	$5.1 \times 10^4$	3.39	0.11
5	$[\text{Ag-S-C}_6\text{H}_4\text{-S-Ag}]_n$	$8.4 \times 10^8$	0.96	0.23
6	$[\text{Ni-S-C}_6\text{H}_4\text{-S-}]_n$	$\sim 10^9$	-----	-----
7	$[\text{Hg-S-C}_6\text{H}_4\text{-S-}]_n$	$\sim 10^9$ (at 60° C)	-----	-----

\*  $E_a$  defined by  $\log \rho = \log \rho_0 + E_a/kT$ .

\*\* Measured in vacuo. All others were measured under argon.

## DISCUSSION:

In their general properties (good thermal and chemical stability and insolubility), the metal complexes of 1,4-dimercaptobenzene reported here closely resemble the mercaptide complexes of palladium(II) previously formulated as S-bridged high polymers of general formula  $[\text{Pd}(\text{SR})_2]_n$ .<sup>18</sup> This formulation is generally accepted for other mercaptide complexes.<sup>19-24</sup> In view of the well-known tendency of the coordinated thiol sulfur to form bridges and the overall similarity to the recently reported Pd(II) complexes of 1,2-ethanedithiol and 1,3-propanedithiol,<sup>25</sup> it would be reasonable to regard the metal complexes of 1,4-dimercaptobenzene of the type  $[\text{M}-\text{S}-\text{C}_6\text{H}_4-\text{S}]_n$  as coordination polymers with the aggregation shown below:



Similar polymeric structures involving sulfur-bridged metal chains are also postulated for metal complexes of the type  $[\text{M}-\text{S}-\text{C}_6\text{H}_4-\text{S}-\text{M}]_n$  ( $\text{M}=\text{Cu}(\text{I})$  and  $\text{Ag}(\text{I})$ ) and  $[\text{C}_6\text{H}_5\text{SCu}]_n$ . Although there is a lack of structural evidence, it is possible that the polymeric chains shown in Figures 1 and 2 are arranged in the

solid state so as to allow the formation of metal-metal bonds which would enhance the ease of intermolecular electron transfer and hence carrier mobilities. The enormously high electrical conductivities of the Cu(I) complexes relative to the M(II) complexes would be in accord with this view.

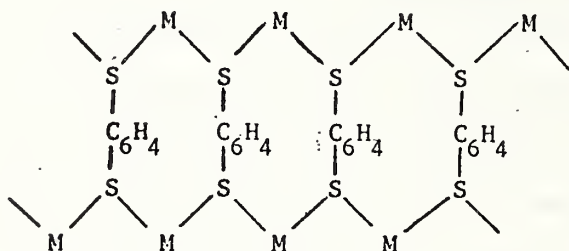


Figure 1.

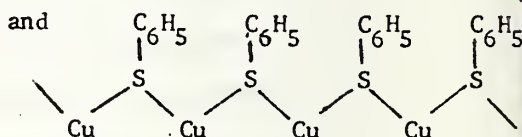


Figure 2.

The high chemical reactivity of the complexes towards organic halides and the ready cleavage of the Cu-S bonds by TCNQ under very mild conditions appear to be consistent with a two-dimensional representation in which coordinated thiol sulfur retains much of its nucleophilic character. It is possible that further cross-linking could lead to a three-dimensional network. However, we believe that further cross-linking would render the thiol sulfur much less reactive towards organic halides. The facile cleavage of the metal mercaptides by organic halides is a reflection of the appreciable nucleophilic character of the coordinated thiol sulfur and, therefore, tends to discount three-dimensional network structures for the complexes reported here.

The resistivities of compressed powder compacts of the mercaptide complexes in the temperature range of 25-100°C fit the expression  $\rho = \rho_0 e^{E_a/kT}$  for the activated conductivity. There was no apparent relationship between thermal activation energies for conduction and the band gap of the form  $2E_a = E_g$ , as required by the intrinsic band model. As the yellow color of many of these



complexes would suggest, the conductivity may be extrinsic and impurity dominated. The impurity, however, need not be foreign and could arise from lattice imperfections. The solid state absorption spectra of the copper complexes in KBr pellets in the range of 3125-14286  $\text{cm}^{-1}$  showed continuous absorption extending into the visible region with onsets at much higher energies than the anticipated optical transition energies based on thermal activation energies for conduction. The onsets, which were neither sharp nor well-defined, occurred at 5714  $\text{cm}^{-1}$  (0.71 eV) for  $[\text{Cu-S-C}_6\text{H}_4\text{-S-Cu}]_n$ ; 4098  $\text{cm}^{-1}$  (0.51 eV) for  $[\text{C}_6\text{H}_5\text{SCu}]_n$ ; and 3683  $\text{cm}^{-1}$  (0.46 eV) for  $[\text{Cu-S-C}_6\text{H}_4\text{-S-}]_n$ . They do not correlate with the band gap calculated from the thermal activation energies for conduction.

The Cu(I) complexes of 1,4-dimercaptobenzene and of thiophenol are better conductors than those of  $\text{Cu}^{++}$  and the other metals studied to date. It is interesting to note that both the electrical conductivities and the thermal activation energies for conduction are markedly influenced by the copper content of the mercaptide complexes. This is shown for the three copper complexes reported here. For example, the Cu(II) complex of composition  $[\text{Cu-S-C}_6\text{H}_4\text{-S-}]_n$  (wt% Cu, 31.01) has a resistivity of  $3.6 \times 10^8 \text{ ohm}\cdot\text{cm}$  and  $E_a = 0.16 \text{ eV}$ , whereas the Cu(I) complex of composition  $[\text{Cu-S-C}_6\text{H}_4\text{-S-Cu}]_n$  (wt% Cu, 47.74) has a resistivity of  $40 \text{ ohm}\cdot\text{cm}$  and  $E_a = 0.054 \text{ eV}$ . The electrical resistivity ( $5.1 \times 10^4 \text{ ohm}\cdot\text{cm}$ ) and the thermal activation energy ( $E_a = 0.11 \text{ eV}$ ) for  $[\text{CuSC}_6\text{H}_5]_n$  (wt% Cu, 36.88) fall between those of the Cu(I) and Cu(II) complexes of 1,4-dimercaptobenzene. This increase in the conductivity and decrease in the thermal activation energies for conduction

with increasing copper content indicate that the conductivity mechanism may involve an interaction of copper 3d-orbitals with the  $\pi^*$  orbitals of the ligand systems. However, the structural variations due to compositional differences should be even more important in influencing the electrical conductivities. As we pointed out earlier, the possible link-up of the polymeric chain structures of the Cu(I) complexes by the Cu-Cu bonds in the solid state would greatly facilitate intermolecular electron transfer. It is therefore likely that the formation of Cu-Cu bonds and the proposed d orbital overlap, which will influence the probability of electron transfer via a tunneling process, or the height of the activation energy barrier for electron hopping<sup>26</sup>, play important roles in determining the electrical conductivities of the copper complexes.

Finally, we mention that the metal mercaptides exhibit visible photoluminescence emissions at room temperature after excitation by 3650 Å: orange for  $[\text{Ag-S-C}_6\text{H}_4\text{-S-Ag}]_n$ ; red for  $[\text{Cu-S-C}_6\text{H}_4\text{-S-Cu}]_n$ ; purple for  $[\text{Cu-S-C}_6\text{H}_4\text{-S-}]_n$  and  $[\text{Hg-S-C}_6\text{H}_4\text{-S-}]_n$ ; and pink-red for  $[\text{C}_6\text{H}_5\text{SCu}]_n$ .

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Figure 3: Temperature dependence of resistivity ( $\rho$ )

○  $[\text{Cu-S-C}_6\text{H}_4\text{-S-Cu}]_n$  (prepared in 2,4-lutidine).

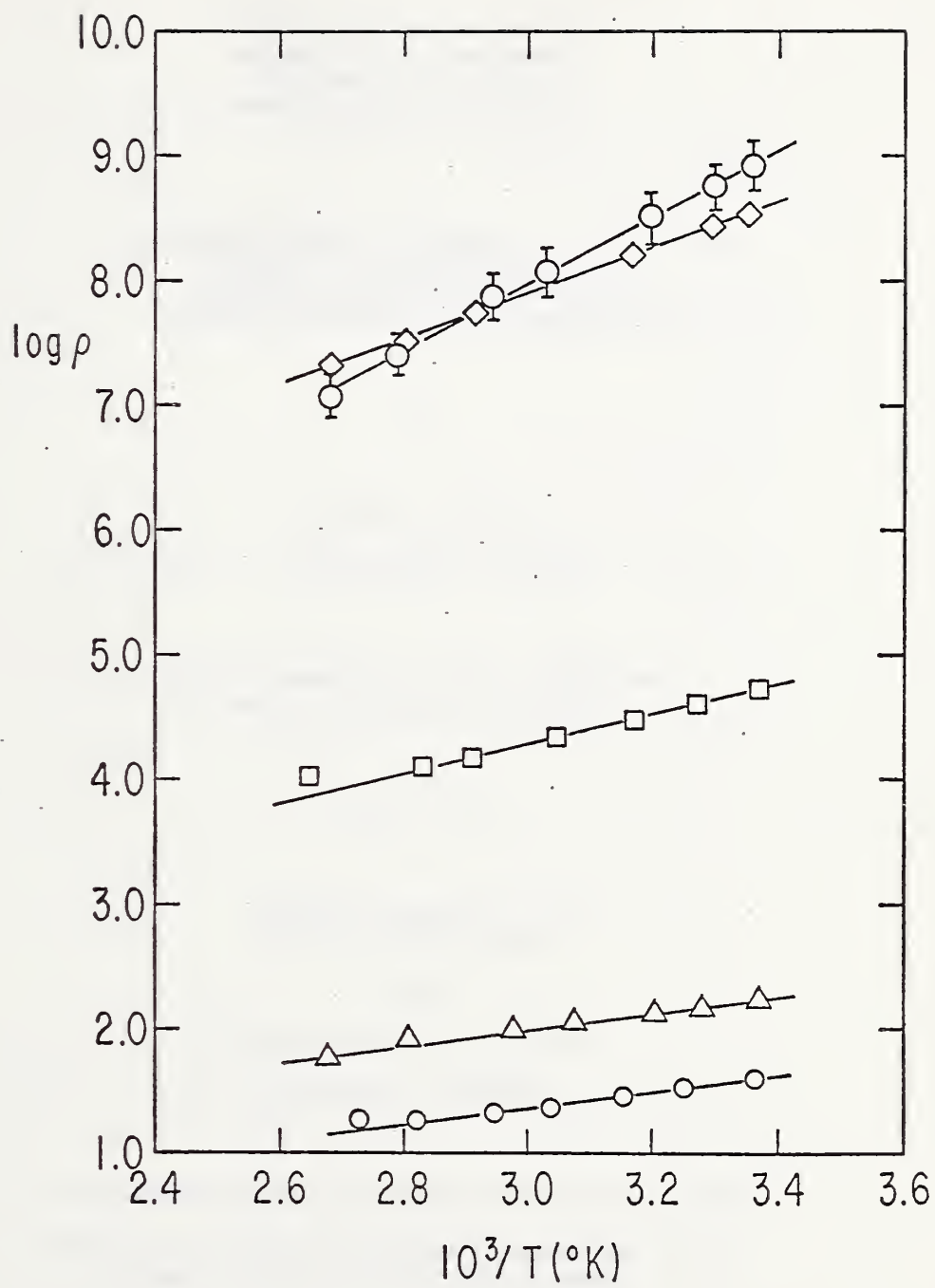
△  $[\text{Cu-S-C}_6\text{H}_4\text{-S-Cu}]_n$  (prepared by solid state reaction).

□  $[\text{C}_6\text{H}_5\text{SCu}]_n$

⊖  $[\text{Ag-S-C}_6\text{H}_4\text{-S-Ag}]_n$

◇  $[\text{Cu-S-C}_6\text{H}_4\text{-S-}]_n$

Fig. 3.





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(HALOMETHYL)ARSENIC COMPOUNDS. I. PRIMARY AND  
SECONDARY (HALOMETHYL)ARSINES II.  
PREPARATION AND CHARACTERIZATION OF  
PENTAKIS(CHLOROMETHYL)CYCLOPENTAARSINE

By

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(HALOMETHYL)ARSENIC COMPOUNDS. I. PRIMARY AND SECONDARY  
(HALOMETHYL)ARSINES

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SUMMARY

(Chloromethyl)arsine,  $\text{ClCH}_2\text{AsH}_2$ , and bis(chloromethyl)-arsine,  $(\text{ClCH}_2)_2\text{AsH}$ , were prepared by the reduction of (chloromethyl)arsonic and bis(chloromethyl)arsinic acids, respectively. (Bromomethyl) and (iodomethyl) analogs of the primary and secondary arsines could not be prepared because of a facile rearrangement from C-functional to As-functional halides. Reactions of  $\text{ClCH}_2\text{AsH}_2$  demonstrated a strongly reduced affinity for proton-proton exchange with hydrogen halide (in comparison to  $\text{CH}_3\text{AsH}_2$ ), a reduction anticipated by group-electronegativity considerations. Nmr, ir, and mass spectral data are included.



## INTRODUCTION

Compounds containing (halomethyl)-substituted metals and metalloids have long interested organometallic chemists as potential carbene precursors and as intermediates in the preparation of methylene-bridged bimetallics [1]. A recent investigation of potentially important non-bonded metal-halogen  $p\pi - d\pi$  interactions in (halomethyl)silanes and -germanes has brought further attention to this important group of compounds [2].

Information about primary (halomethyl) derivatives of metals possessing non-bonding electron pairs (groups V and VI) is limited to a single substantiated example\*: (chloromethyl)phosphine,  $\text{ClCH}_2\text{PH}_2$  [4,5]. The presence of non-bonding electron pairs on the central atom presents additional possibilities (both attractive and repulsive) for "across-space" metal-halogen interactions. This paper reports the preparation and properties of two new compounds: (chloromethyl)arsine,  $\text{ClCH}_2\text{AsH}_2$ , and bis(chloromethyl)-arsine,  $(\text{ClCH}_2)_2\text{AsH}$ , and the significant failure to prepare (bromomethyl) and (iodomethyl) analogs.

## RESULTS AND DISCUSSION

### Preparation and Characterization of $\text{XCH}_2\text{AsH}_2$ Compounds

$\text{ClCH}_2\text{AsCl}_2$ , obtained from the diazomethane- $\text{AsCl}_3$  insertion reaction [6,7], could not be directly reduced to  $\text{ClCH}_2\text{AsH}_2$ . Reducing agents employed were  $\text{Zn/HCl}$ ,  $\text{Zn/H}_2\text{SO}_4$ ,  $\text{NaBH}_4$  or  $\text{LiAlH}_4$ ;

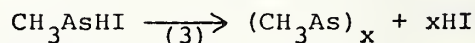
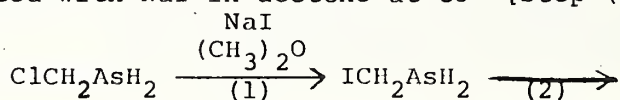
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\*A claim has been made for the preparation of (chloromethyl)amine,  $\text{ClCH}_2\text{NH}_2$ , but only decomposition products were isolated [3].

the  $\text{NaBH}_4$  reactions were conducted in both  $\text{H}_2\text{O}$  and n-butyl ether, and  $\text{LiAlH}_4$  in n-butyl ether. In all cases no more than trace amounts (less than 1%) of  $\text{ClCH}_2\text{AsH}_2$  were obtained. When  $\text{ClCH}_2\text{AsCl}_2$ , however, is first oxidized with 15%  $\text{H}_2\text{O}_2$  to the arsonic acid,  $\text{ClCH}_2\text{AsO}(\text{OH})_2$ , and then reduced by the  $\text{Zn}/\text{H}_2\text{SO}_4$  couple, a 65% yield of  $\text{ClCH}_2\text{AsH}_2$  is obtained. Similarly, oxidation of  $(\text{ClCH}_2)_2\text{AsCl}$  produced  $(\text{ClCH}_2)_2\text{AsO}(\text{OH})$  which affords the corresponding secondary arsine in 10% yield on  $\text{Zn}/\text{H}_2\text{SO}_4$  reduction.

Likewise,  $\text{BrCH}_2\text{AsBr}_2$  failed to yield  $\text{BrCH}_2\text{AsH}_2$  on direct reduction, but in this case the cause of failure includes the inherent instability of the product (see below). Also, attempts to oxidize  $\text{BrCH}_2\text{AsBr}_2$  to  $\text{BrCH}_2\text{AsO}(\text{OH})_2$  with 15%  $\text{H}_2\text{O}_2$  were accompanied by the strong evolution of bromine; no arsonic acid could be isolated from the reaction products.

In an attempt to prepare (iodomethyl) arsine,  $\text{ClCH}_2\text{AsH}_2$  was treated with  $\text{NaI}$  in acetone at  $35^\circ$  [step (1)]. The desired

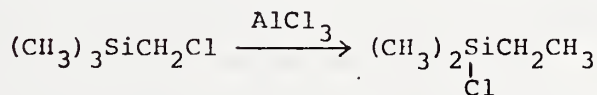


product,  $\text{ICH}_2\text{AsH}_2$ , was not obtained; observations during the course of the reaction suggested that the product spontaneously rearranged to an arsenic-functional iodide [step (2)], which itself has previously been shown [10] to disproportionate to polyarsines and  $\text{HI}$  [step (3)]. This was evidenced by the solution's rapid

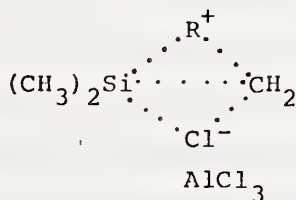
Intensification of yellow-orange coloration accompanied by a considerable amount of brick-red precipitate analyzed as  $(\text{CH}_3\text{As})_x$ . No evidence for free  $\text{I}_2$  was observed during the rearrangement. These results also correlate well with thermal

rearrangements observed in  $\text{ICH}_2\text{GeH}_3$ , where  $\text{CH}_3\text{GeH}_3$  and  $\text{GeI}_4$  were observed, among other products [8]. Although the germanium rearrangements could be catalyzed by light, the arsenic reactions were completely shielded from light.

The rearrangement (step 2) can be conveniently viewed as an elimination/addition of HI through an intermediate of the type  $\text{CH}_2=\text{AsH}$  (which surely would exist primarily as  $^{\ominus}\text{CH}_2-\text{AsH}^{\oplus}$ ); no evidence for or against its presence was found. Goldwhite has suggested  $\text{CH}_2=\text{PH}$  as an intermediate in the alkaline hydrolysis of  $\text{ClCH}_2\text{PH}_2$ . [4] A similar rearrangement of (chloromethyl)trimethylsilane, although catalyzed by aluminum chloride,



is thought to occur through a doubly-bridged intermediate [9].



Since it is known that  $\text{CH}_3\text{AsHI}$  can exist only in equilibrium with  $\text{CH}_3\text{AsH}_2$  and  $\text{CH}_3\text{AsI}_2$  [10], the formation of polyarsine (step 3),

may include condensation of  $\text{CH}_3\text{AsH}_3$  with either  $\text{CH}_3\text{AsH}_2$  or  $\text{CH}_3\text{AsI}_2$  in addition to self-condensation.

#### Proton Magnetic Resonance Spectra

(Chloromethyl)arsine: The 60 MHz pmr spectrum of (chloromethyl)arsine is shown in Fig. 1. Spectral parameters tabulated in Table 1 were obtained from a modified LAOCOON III computer-generated "best-fit" spectra, with the assumption that free rotation about the C-As bond would allow assignment of the molecule to the spin system,  $\text{AA}'\text{BB}'$  [11]. While normal  $\text{AA}'\text{BB}'$  spectra exist in two mirror-image halves which can lead to difficulties in assigning the A and B proton sets, the up-field half of the spectrum in Fig. 1 clearly shows the effects of quadrupolar broadening from  $^{75}\text{As}$  ( $I=3/2$ , 100% abundant). The up-field half is therefore assigned to protons directly bonded to arsenic. The pmr data for  $\text{ClCH}_2\text{AsH}_2$  in Table 1 derive from iteratively converged, observed and calculated, line positions with a satisfactory resultant RMS error of 0.047.

While the error figure demonstrates that the calculated line positions produce a good fit, deviations in line intensities of up to 20% were observed, possibly because of a failure of the initial assumption of free C-As bond rotation. To test this possibility the spin system was changed from  $\text{AA}'\text{BB}'$  (free rotation) to ABCD (restricted rotation) and further calculations performed. The introduction of anisochronous chemical shifts ( $\pm 1.0$  Hz from the  $\text{AA}'\text{BB}'$  best fit values) produced, of course, many additional calculated lines but all new lines were of very weak intensity

and did not appreciably alter the envelope of observed spectral lines. The possibility of restricted rotation was further tested by examining spectra of  $\text{ClCH}_2\text{AsH}_2$  in t-butylbenzene through the temperature range  $-100$  to  $110^\circ$ . While temperature-dependent changes in  $\Delta\nu(\text{AB})$  ( $5 \text{ Hz @ } -100^\circ$ ;  $45 \text{ Hz @ } 110^\circ$ ) and the effects of quadrupolar broadening (almost no broadening at  $-100^\circ$ ) were found, there was no indication of restricted rotation. The line intensity discrepancies may be the simple result of unequal (but small) quadrupolar broadening of the individual lines of the methylene half of the spectrum [12]. An inherent ambiguity arises in the assignment of the two geminal coupling constants,  $J(\text{HAsH})$  and  $J(\text{HCH})$ . Consequently, comparison must be made to known values, and use made of any additional spectral information before assignment is possible. Although no  $J(\text{HAsH})$  values have been previously reported, several  $J(\text{HPH})$  values are available. The seemingly close relationship between H-N-H couplings and H-P-H couplings (see below) provides some assurance that trends could, with appropriate caution, be extended to H-As-H couplings.

The reported values of H-N-H and H-P-H couplings are (in Hz):  $\text{NH}_3$ ,  $-10.35$  [13];  $\text{NH}_4^+$ ,  $-11.67$  [14];  $\text{CH}_3\text{NH}_2$ ,  $-13.23$  (predicted [15]);  $\text{PH}_3$ ,  $-13.45$  [16];  $\text{CH}_3\text{PH}_2$ ,  $-12.46$  [17];  $\text{CF}_3\text{PH}_2$ ,  $-13.37$  [18];  $\text{C}_6\text{H}_5\text{PH}_2$ ,  $-13.11$  [17]. It is reasonable, therefore, to assign the  $-16.99 \text{ Hz}$  geminal coupling to H-As-H. On the basis of the foregoing results the sign assigned to  $J(\text{HPH})$  in  $\text{ClCH}_2\text{PH}_2$  [5] must be in error. (See Table 1.)



The other geminal value,  $-1.28$  Hz, is then  $J(\text{HCH})$ . Experimental evidence suggests that  $J(\text{HCH})$  increases algebraically as the  $\text{H-C-H}$  bond angle widens [19]. Tetrahedral acyclic carbon systems generally give rise to geminal couplings in a rather narrow range from  $-15$  to  $-10$  Hz, with a few values falling just outside this range, and  $\text{sp}^2$  hybridized carbon generally produces geminal couplings a little to either side of zero.

It is also well noted that  $J(^{13}\text{C-H})$  is quite sensitive to changes in  $s$ -character of the carbon bonding orbitals [20]; increase in  $s$ -character leads, in general, to an increase in  $J(^{13}\text{C-H})$ .  $\text{sp}^3$  carbon normally provides couplings between 125 (methane, cyclohexane) and 175 Hz (methylene dihalides).  $J(^{13}\text{C-H})$  for  $\text{ClCH}_2\text{AsH}_2$  is 157.8 Hz, which is within the region for electro-negatively-substituted  $\text{sp}^3$  carbon, but nonetheless is a rather high value. Correlation is then seen between  $J(\text{HCH})$  and  $J(^{13}\text{C-H})$ ; each is sensitive to carbon  $s$ -character, and in the case of  $\text{ClCH}_2\text{AsH}_2$ , both values indicate a high degree of  $s$  character in carbon's bonds to hydrogen. The consequently narrowed  $\text{Cl-C-As}$  bond angle may be an indication of an attractive  $\text{As}\cdots\text{Cl}$  interaction and/or a demonstration of the tendency for  $p$ -character to concentrate in bonds to electronegative substituents (Bent's Rule [21]).

In group-V systems a potential exists for both halogen and group-V element  $d$ -orbital involvement in lone-pair delocalization; the net result could either increase or decrease the net lone-pair electron density, and therefore, either augment or detract

from the  $\sigma$ -electron-withdrawing effect of the (chloromethyl) group. Both  $J(\text{H-C-H})$  and  $J(^{13}\text{C-H})$  for  $\text{ClCH}_2\text{AsH}_2$  support an attractive  $\text{Cl}\dots\text{As}$  interaction, and the strongly reduced affinity for proton-proton exchange with hydrogen halide of  $\text{ClCH}_2\text{AsH}_2$  (compared to  $\text{CH}_3\text{AsH}_2$ ) suggests that if  $d$ -orbital participation is significant in this interaction, it is chlorine, not arsenic, that participates.\* It is difficult, however, to account for the apparent absence (from nmr coupling constants) of similar effects in  $\text{ClCH}_2\text{PH}_2$ .

Bis(chloromethyl)arsine: The 100 MHz pmr spectrum of  $(\text{ClCH}_2)_2\text{AsH}$ , obtained as a by-product of the preparation of  $\text{ClCH}_2\text{AsH}$ , is shown in Fig. 2. All attempts to perform a complete analysis of spectral parameters proved futile because of insufficient resolution of individual lines arising from 1) uncertain assignments of quadrupolar broadened lines, 2) similarity of the absolute magnitude of chemical shift differences and coupling constants, and 3) the chemical non-equivalency of the two protons on each methylene group. Nonetheless, based on the spin system assignment  $\text{AA}'\text{BB}'\text{C}$ , approximate chemical shifts given in Table I were determined by the bold assumption that the relevant coupling constants in  $\text{ClCH}_2\text{AsH}_2$  remain unchanged in  $(\text{ClCH}_2)_2\text{AsH}$ .

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\*M.O. calculations support this conclusion [22]. Further, an estimated group electronegativity difference of about 0.2 between methyl and chloromethyl [23] seems too small to account for the profound change in basicity.

### Mass Spectrum of ClCH<sub>2</sub>AsH<sub>2</sub>

The mass spectrum of ClCH<sub>2</sub>AsH<sub>2</sub>, shown in Table 2, was obtained at an ionizing voltage of 70 eV and an ionizing chamber pressure of  $2 \times 10^{-6}$  mmHg. Some features of the spectra require special comment. The base peak, m/e 90, suggests a process involving loss of the elements of HCl to yield CH<sub>2</sub>AsH<sup>+</sup>. Since it is frequently possible to show good agreement between thermal and electron-impact decompositions, it is noteworthy that the structural isomer, CH<sub>3</sub>AsHCl, decomposes thermally with the loss of HCl. [10] The base peak in the spectrum of CH<sub>3</sub>AsH<sub>2</sub> is also at m/e 90, but the spectrum of CD<sub>3</sub>AsH<sub>2</sub> demonstrates that both arsenic-bonded hydrogens are lost preferentially [24].

The peaks at m/e 110-113 represent rearrangements involving formation of As-Cl bonds. Identical rearrangements have been found in  $\alpha$ -halosilanes and -germanes [2b]. Dobbie and Cavell have found similar and extensive rearrangement in the spectra of CF<sub>3</sub>-substituted phosphines and arsines [25]. They attribute the rearrangement process to an initial interaction between the fluorine p orbitals and the unoccupied d orbitals of the metalloid, and they strengthen their argument by citing earlier work which indicated that CF<sub>3</sub>-substituted amines did not show these rearrangement peaks [26].

### Infrared Spectra

(Chloromethyl)arsine is expected to possess C<sub>s</sub> symmetry, the symmetry plane being described by the heavy atoms. It proved

useful in assigning observed absorptional frequencies to the fundamental modes to examine the rotation-vibration band contours of vapor-phase spectra [27].

In the spectra for  $\text{ClCH}_2\text{AsH}_2$  (see Table 3), the complex band at  $2900\text{--}3000\text{ cm}^{-1}$  must include both a symmetric and an antisymmetric C-H stretching band. While the resolution in the infrared spectra is not sufficient to assign the bands on the basis of contour characteristics alone, analogy can be made to Raman depolarization data from related compounds [28]. Thus, in methylarsine the antisymmetric mode is found at higher frequency.

Two bands are expected for the As-H stretching vibrations: one symmetric, giving rise to an A-B hybrid band contour; the other antisymmetric, giving rise to a C band. The complex band at  $2050\text{--}2150\text{ cm}^{-1}$  surely contains both modes, but again unambiguous assignment of the observed frequencies to expected modes does not seem possible without Raman corroboration. The weak band centered at  $1410\text{ cm}^{-1}$  is characteristic of the methylene group and is attributed to the  $\text{CH}_2$  scissors vibration. No rotational character is observed. Other bands characteristic of the methylene group are observed in the region above  $1000\text{ cm}^{-1}$ . The wagging mode, an A' vibration centered at  $1188\text{ cm}^{-1}$ , has the expected A-B hybrid envelope. The  $\text{CH}_2$  twist occurs at  $1108\text{ cm}^{-1}$  and is weak, but exhibits the type C envelope expected of an A" vibration.

The band centered at  $963\text{ cm}^{-1}$  bears a strong type C resemblance (perhaps evidence for the molecule being a nearly symmetric rotor), but must be the A-B hybrid expected for the As-H scissor vibration. This mode is observed at  $973\text{ cm}^{-1}$  in methylarsine [28]. In a number of methylarsine derivatives, the  $\text{AsH}_2$  twisting and wagging vibrations show strong interactions and usually appear within  $20\text{ cm}^{-1}$  of each other [28]. The wagging vibration will produce an A-B hybrid envelope, while the antisymmetric twisting mode is expected to produce a band of type C. The complex envelope at  $760\text{--}800\text{ cm}^{-1}$  is thought to contain both modes, the absence of adequate resolution again prevents an unambiguous assignment.

The band centered at  $862\text{ cm}^{-1}$  is of type C and is attributed to the antisymmetric  $\text{AsH}_2$  rocking mode. The C-Cl stretching vibration displays essentially a B type envelope and is centered at  $727\text{ cm}^{-1}$ . The antisymmetric  $\text{CH}_2$  rocking vibration is located at the shoulder centered at  $700\text{ cm}^{-1}$ . This assignment is tentative. The assignments are summarized in Table 3. The C-As stretching vibration must be incorporated in the group of absorptions in the region from  $500\text{--}550\text{ cm}^{-1}$ , but the absence of an obvious contour type prevents the designation of a specific band origin. The skeletal deformation mode is likely in the region near  $200\text{ cm}^{-1}$ , but could not be observed.

#### Reaction of $\text{ClCH}_2\text{AsH}_2$ and $\text{I}_2$

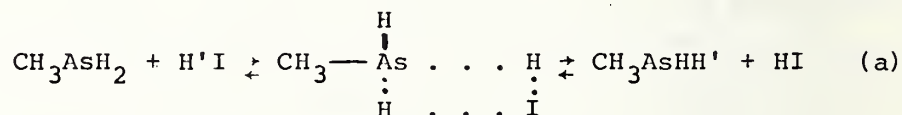
Nmr studies of the reactions of  $\text{CH}_3\text{AsH}_2$  and  $\text{I}_2$  in benzene followed for considerable periods of time (up to 3 yrs.) show a



slow, but remarkable, succession of changes in reaction mixture composition [10,29]. Initially,  $\text{CH}_3\text{AsHI}$ ,  $\text{CH}_3\text{AsI}_2$  and  $\text{HI}$  are rapidly formed on iodine decolorization (immediately following solution thawing). When the  $\text{CH}_3\text{AsH}_2/\text{I}_2$  ratio is initially one or greater, excess  $\text{CH}_3\text{AsH}_2$  is also seen. At later times measurable quantities of  $\text{H}_2$  are formed, and simultaneous with the maximum in  $\text{H}_2$  pressure (3 to 9 mos.), the concentration of  $\text{HI}$  becomes undetectable. At this time a new, broad nmr signal appears at 8.04  $\tau$  and is attributed to a family of iodine-terminated, benzene-soluble polyarsines,  $\text{I}-(\text{AsCH}_3)_x-\text{I}$ . At still longer times, 1.5 to 3 yrs., precipitation of a purple-black, essentially halogen-free ladder polymer of empirical formula,  $\text{CH}_3\text{As}$ , commences. Suggestions of mechanisms which satisfactorily explain these observations have appeared elsewhere [29]. It was hoped that the details of these mechanistic proposals might be tested by comparing the  $\text{CH}_3\text{AsH}_2/\text{I}_2$  reactions with ones utilizing  $\text{ClCH}_2\text{AsH}_2$ , where the greater electronegativity of the chloromethyl group would offer predictable quantitative differences.

At  $\text{ClCH}_2\text{AsH}_2/\text{I}_2$  molar ratios of 3:1 and 3:2 in benzene solution in sealed tubes,  $\text{I}_2$  was decolorized at a rate too fast to follow by nmr. Immediately formed are  $\text{ClCH}_2\text{AsHI}$ ,  $\text{ClCH}_2\text{AsI}_2$ ,  $\text{HI}$  and, at both molar ratios, excess  $\text{ClCH}_2\text{AsH}_2$ . The proportion of iodinated products is greater at the smaller molar ratio. Considerable overlap of the complex nmr patterns for  $\text{ClCH}_2\text{AsH}_2$  (AA'BB') and  $\text{ClCH}_2\text{AsHI}$  (ABC) (see Table 1 for spectral parameters) made difficult the retrieval of quantitative data from integrated peak-area ratios.

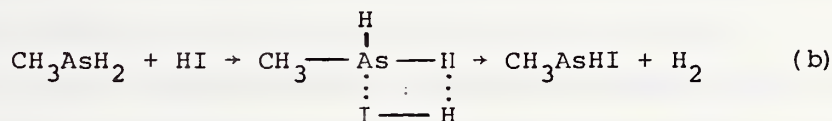
A striking feature of the spectra from the  $\text{CH}_3\text{AsH}_2/\text{I}_2$  system prior to HI depletion is the spectral appearance of excess  $\text{CH}_3\text{AsH}_2$ . Rather than the triplet-quartet pattern exhibited by  $\text{CH}_3\text{AsH}_2$  alone in benzene, the total spectrum for excess  $\text{CH}_3\text{AsH}_2$  in the iodine systems is a single line coincidental with the central line of the anticipated methyl triplet. If  $\text{CH}_3\text{AsH}_2$  is rapidly exchanging its arsenic-bonded protons with another compound far removed in chemical shift from  $\nu(\text{AsH}_2)$ , then the  $\text{AsH}_2$  quartet could broaden sufficiently to merge with the baseline, and the multiplicity of the  $\text{CH}_3$  triplet would collapse to a singlet. Based upon an independent study of the interaction of HI and  $\text{CH}_3\text{AsH}_2$ , it is concluded that the distortions in the  $\text{CH}_3\text{AsH}_2$  spectrum in  $\text{I}_2$  systems result from exchange with HI [10].



Significantly, the  $\text{ClCH}_2$  spectral system of  $\text{ClCH}_2\text{AsH}_2$  shows no indication of the proton-proton exchange broadening or multiplicity collapse found in the  $\text{CH}_3\text{AsH}_2/\text{I}_2$  systems. Thus, the rate for such exchange must be at least two orders of magnitude slower on the  $\text{ClCH}_2\text{As}<$  moiety, as would be anticipated by the reduced basicity of  $\text{ClCH}_2\text{AsH}_2$ , assuming that the mechanism for exchange reflects the availability of the As lone pair. If, as proposed earlier, the exchange intermediate is four-centered (a),

then the rate-determining step may be proton (from HI) attack on arsenic as in quaternization mechanisms, and thus related to lone-pair availability. We have determined activation parameters for HI proton exchange with  $(\text{CH}_3)_2\text{AsH}$ ; most significant is  $\Delta S^\ddagger = -45.1 \text{ J mol}^{-1} \text{ deg}^{-1}$ , suggestive of an associative, quaternization-like mechanism [29].

The first appearance of polyarsine\* peaks in the  $\text{CH}_3\text{AsH}_2/\text{I}_2$  systems is accompanied by a permanent maximum in  $\text{H}_2$  pressure and a disappearance of HI (as evidenced by a return of the complete quartet-triplet spectrum for  $\text{CH}_3\text{AsH}_2$ ). This is explicable in terms of an irreversible consumption of HI through reaction with  $\text{CH}_3\text{AsH}_2$ , and requires a different orientation of the HI molecule with  $\text{CH}_3\text{AsH}_2$  than shown in equation b, e.g.,



Since the ability of HX to cleave As-As bonds increases rapidly with halogen atomic weight, polyarsine formation is inhibited until all HI is consumed.

If the rate of arsyl-HX proton-proton exchange is greatly diminished for reasons of decreased lone-pair availability when  $\text{ClCH}_2\text{AsH}_2$  replaces  $\text{CH}_3\text{AsH}_2$ , then the rate of  $\text{H}_2$  production (therefore also HI consumption and polyarsine formation) would

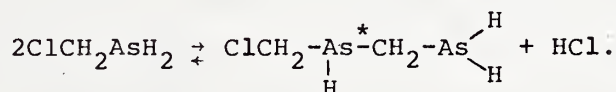
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\*Defined herein as meaning a degree of catenation greater than two.

be anticipated to be greater when  $R = \text{ClCH}_2$  in (b) due to a stronger As...I interaction. In confirmation of these predictions we find that the rate of  $\text{H}_2$  evolution and the onset of observable polyarsine formation occurs about 40-50 times faster when  $R = \text{ClCH}_2$ ; when  $R = \text{CH}_3$ , polyarsine onset does not occur for up to nine months; whereas, when  $R = \text{ClCH}_2$ , in systems of an identical initial As/I ratio, polyarsine onset occurs at 6 days.

In the 3:2 system, the concentrations of  $\text{ClCH}_2\text{AsH}_2$  and  $\text{ClCH}_2\text{AsHI}$  decrease slowly, and after 6 days at  $60^\circ$   $\text{ClCH}_2\text{AsH}_2$  disappears completely, while the concentration of  $\text{ClCH}_2\text{AsI}_2$  very gradually increases (very much like the methylarsine reactions at similar reactant ratios). At 6 days two new peaks appear at 6.16 and 9.72  $\tau$ . The lower-field peak is close to that of pentakis(chloromethyl)cyclopentaarsine (av. 6.00  $\tau$ ) [30] and may possibly be due to a condensed As-As bonded compound of the form  $\text{ClCH}_2(\text{I})\text{AsAs}(\text{I})\text{CH}_2\text{Cl}$ , a different diarsine, or a polyarsine of greater complexity. In the methylarsine systems the open-chain polyarsine resonance was found 0.35 ppm downfield from that of  $(\text{CH}_3\text{As})_5$ . [10] If the assignment of the 6.16  $\tau$  peak is correct, explanation of the opposite relationship of linear vs. cyclic chemical shifts may reflect the steric requirements of the  $\text{ClCH}_2$  group in addition to electronegativity effects. Space-filling models predict a reduction in As-As-As bond angle on shifting from linear to cyclic forms for the chloromethyl derivatives, and the reverse for the methyl derivatives.

The infinite-dilution chemical shift of HCl in benzene is 9.86  $\tau$  and moves downfield to about 9.2  $\tau$  when saturated. HCl could either derive from a thermal rearrangement of one of the  $\text{ClCH}_2\text{As}<$  compounds, or from Cl abstraction by a kind of intermolecular quaternization, i.e.,



Recleavage of the starred internal C-As bond by HCl would afford  $\text{ClCH}_2\text{AsHCl} + \text{CH}_3\text{AsH}_2$  by a process similar to that described above for  $\text{ICH}_2\text{AsH}_2$ . Regardless of mechanism, the presence of HCl does not interfere with As-As bond formation as does HI, and its presence can account for the 9.72  $\tau$  peak. Pure samples of  $\text{ClCH}_2\text{AsH}_2$  in benzene show no tendency to form HCl even on prolonged storage at 60°.

Contrary to  $\text{CH}_3\text{As}<$  systems, the 6.16  $\tau$  peak shows a slow decline with time but at 13 days is joined by three new peaks at 5.32, 6.41, and 6.85  $\tau$  which may also be polyarsine modifications. The summed intensities of the four peaks attributed to polyarsines show an increase with time. Whereas in  $\text{CH}_3\text{As}<$  systems (when the halogen is iodine) the polyarsine peak is always a somewhat broadened single peak due to intermolecular exchange of parts, the bromine reactions show polyarsine peaks resolved into several component resonances from a reduced rate of exchange [28]. Similarity is seen in the increase in the electronegativity from iodine to bromine, and  $\text{CH}_3$  to  $\text{ClCH}_2$ :



both reduce the availability of the non-bonding pair for associative interactions. The rate of intermolecular exchange of polyarsine parts is, therefore, also an apparent function of lone-pair density.

As a further indication of polyarsine formation, a slight but increasing amount of orange precipitate is formed during the course of the reaction. A chemically similar orange solid occurs as a by-product of all preparative routes to  $(\text{ClCH}_2\text{As})_5$  and likely is related to the red-brown solid frequently found in association with  $(\text{CH}_3\text{As})_5$  [30].

#### EXPERIMENTAL

Volatile, air-sensitive materials were handled in an all-glass vacuum system of standard design. Nmr spectra were recorded on either a Varian A60A or a Perkin-Elmer R20B in sealed tubes; chemical shifts and coupling constants were obtained from minimum sweep-width spectra and represent the average of normally no fewer than five spectra. Mass spectra were recorded on a Varian M-66 and a duPont 21-492; air-sensitive samples and all gases were introduced through an unheated inlet system fitted through the liquid-sample port. The ir spectrum was recorded on a Perkin-Elmer 225 using a 10-cm pathlength gas cell fitted with CsBr windows.  $\text{AsCl}_3$  (Fisher Scientific) was distilled before use;  $\text{AsBr}_3$  and  $\text{ClCH}_2\text{POCl}_2$  (both Alfa Inorganics) were used as obtained.

### Chloromethylarsonic acid and Bis(chloromethyl)arsinic acid

The arsonic acid,  $\text{ClCH}_2\text{AsO}(\text{OH})_2$ , was obtained from  $\text{ClCH}_2\text{AsCl}$  [7] by 15%  $\text{H}_2\text{O}_2$  oxidation [6]. Although elemental analyses showed consistently correct Cl:C:As ratios, variable H content suggested that this arsonic acid, according to the details of synthesis and purification (recrystallization), acquired varying numbers of water molecules of hydration. Similarly,  $(\text{ClCH}_2)_2\text{As}^{\text{O}}(\text{OH})$  was obtained from  $(\text{ClCH}_2)_2\text{AsCl}$  by 15%  $\text{H}_2\text{O}_2$  oxidation.

### (Chloromethyl)arsine

A standard preparation of primary arsines (Zn/HCl reduction of an arsonic acid) [31] was modified by using  $\text{H}_2\text{SO}_4$  instead of HCl and by minimizing the arsonic acid solution concentration by slow addition, a technique found important in maximizing arsine yields in related reductions of  $\text{As}_2\text{O}_3$  [32]. These modifications are also noteworthy because of the complete absence of As-mirror or subhydride formation which often accompany Zn/HCl reductions of As(V) acids.

Volatile products were removed to the vacuum system over a 30-hr period passing first through a  $-78^\circ$  trap then into a  $-196^\circ$  trap. The  $-196^\circ$  trap contained small quantities of  $\text{AsH}_3$  and  $\text{CO}_2$  as identified by their vapor-phase ir spectra. The  $-78^\circ$  trap contained  $\text{ClCH}_2\text{AsH}_2$  (61% yield based upon  $\text{ClCH}_2\text{AsCl}_2$ ). Small quantities of  $\text{H}_2\text{O}$  were removed after condensation on  $\text{P}_4\text{O}_{10}$ . Ideal-gas-law molecular weight of the purified product was 125.5 (calcd. 126.4). The vapor pressure data for  $\text{ClCH}_2\text{AsH}_2$  in the

temperature range, -47.5 to 13.2 is represented by  $\log_{10} P(\text{mm}) = -1690.31^\circ\text{K}^{-1} + 7.48407$ , and yield an extrapolated normal b.p. of  $94.0^\circ$  and heat of vaporization of  $-32.31 \text{ kJ mol}^{-1}$ . The extrapolated b.p. compares reasonably with  $\text{ClCH}_2\text{PH}_2$ ,  $68^\circ$  [4]. Because of its tendency to dissolve in mercury, a separate sample was used for each vapor pressure measurement. (Chloromethyl)arsine is a colorless liquid which shows no thermal instability after one-year storage at room temperature. The nmr, ms and ir data are given in Tables 1-3.

#### Bis(chloromethyl)arsine

$(\text{ClCH}_2)_2\text{AsH}$  was obtained in small quantities as an occasional by-product of the procedure described <sup>above</sup> ~~in part c.~~ Insufficient quantities were available for vapor pressure measurements. Like  $\text{ClCH}_2\text{AsH}_2$ ,  $(\text{ClCH}_2)_2\text{AsH}$  is a colorless liquid of high thermal stability. The nmr spectral data are given in Table 1.

#### (Chloromethyl)phosphine

$\text{ClCH}_2\text{PH}_2$  has been prepared by the thermal decomposition of (chloromethyl)phosphinic acid [4], a not easily accessible starting material. Although we found that commercially available  $\text{ClCH}_2\text{POCl}_2$  could be reduced with  $\text{LiAlH}_4$  in butylether to  $\text{ClCH}_2\text{PH}_2$  in 15% yield, we also found that the yield can be tripled if  $\text{ClCH}_2\text{POCl}_2$  is first converted to  $\text{ClCH}_2\text{PO}(\text{OCH}_3)_2$ .

To 10.8 g (0.1 mol)  $\text{NaOCH}_3$  suspended in 50 ml butylether was slowly added 16.75 g  $\text{ClCH}_2\text{POCl}_2$  in 100 ml butylether at  $0^\circ$ . After warming to room temperature, the solution was filtered and placed

in a 1000 ml, 3-neck flask attached to the vacuum line. To this was slowly added 2 g  $\text{LiAlH}_4$  suspended in 150 ml butylether at  $-20$  to  $-30^\circ$ . Volatile products were removed periodically for 24 hours. 2-ethoxy-ethanol (10 ml) was then added to destroy excess  $\text{LiAlH}_4$  and any  $\text{LiAl}(\text{PHCH}_2\text{Cl})_4$  [33] that had formed. Following fractional condensation purification of the crude product, 3.7 g  $\text{ClCH}_2\text{PH}_2$  (45% yield based on  $\text{ClCH}_2\text{POCl}_2$ ), confirmed by its molecular weight and spectral properties [4] was obtained. Small quantities of  $\text{PH}_3$  and  $\text{CH}_3\text{Cl}$  were removed during purification. The initial attempt at this reduction was conducted at room temperature; the yield was only 10% and a large quantity of  $\text{CH}_3\text{Cl}$  was obtained, presumably the result of C-P bond cleavage.

#### Attempted Synthesis of (Iodomethyl)arsine

Into a 5 ml tube attached to the vacuum system containing a 0.5 g of NaI (dried 2 hrs @  $300^\circ$ ), 1.4 ml of dried acetone and 0.835 mmol  $\text{ClCH}_2\text{AsH}_2$  were distilled. The mixture was held at  $35^\circ$  in the absence of air for 8 hrs during which time a progressively heavier coating of an orange-brown solid collected on the tube wall above the acetone level. Both its appearance and elemental analysis showed this material to approximate  $(\text{CH}_3\text{As})_x$ , an amorphous, possibly linear, high-molecular-weight polymer. After complete acetone removal in vacuo, a small quantity of a pale yellow liquid (presumed to be  $\text{ICH}_2\text{AsH}_2$ ) distilled from the reaction tube. During its passage to a collection trap, more

orange-brown solid was deposited. Only HI (identified only by its molecular weight) was recovered from the trap (see text for discussion).

#### Reaction of $\text{ClCH}_2\text{AsH}_2$ and $\text{I}_2$

In two separate 5 mm nmr tubes, each containing thoroughly degassed and frozen solutions of 0.076 g  $\text{I}_2$  (0.30 mmol) in 0.6 ml benzene (freshly distilled from  $\text{LiAlH}_4$ ), were condensed (at  $-196^\circ$ ) 0.45 or 0.90 mmol  $\text{ClCH}_2\text{AsH}_2$  to yield final  $\text{ClCH}_2\text{AsH}_2/\text{I}_2$  ratios of 1.5:1 and 3:1. Each ratio was prepared in triplicate as a check for consistency. Each tube also contained 0.30 mmol of TMS as both an integration and chemical shift standard. Iodine was decolorized completely as each tube warmed to the solution melting pt (about  $0^\circ$ ), whereupon the first nmr spectrum was obtained. Between spectra the tubes were stored at  $60^\circ$  in a thermostatted oven. Spectra were recorded at intervals sufficiently often to follow completely all observable chemical events. At a time dependent upon the initial As/I ratio (see text for details) varying quantities of orange solid began to deposit on the tube walls.

#### ACKNOWLEDGEMENT

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TABLE 1

PROTON NMR DATA<sup>a</sup>

Compound	$\tau$ (CH)	$\tau$ (AsH)	$J$ (HCH) <sup>b</sup>	$J$ (HEH) <sup>b</sup>	$J$ (HCEH) <sup>b</sup>
$\text{ClCH}_2\text{AsCl}_2$	6.77				
$\text{ClCH}_2\text{AsBr}_2$	6.32				
$\text{ClCH}_2\text{AsI}_2$	6.01				
$\text{ClCH}_2\text{AsHI}$	6.72 6.67	6.56	c		6.3 4.2
$(\text{ClCH}_2)_2\text{AsH}$	6.6 6.7	7.0			
$\text{ClCH}_2\text{AsH}_2$ <sup>d</sup>	6.84	6.54	-1.28	-16.99	7.09 4.65
$\text{ClCH}_2\text{PH}_2$ <sup>d,e</sup>	6.38	6.65	9.8 <sup>f</sup>	10.4 <sup>f</sup>	10.2 4.9

<sup>a</sup>all spectra recorded in benzene except as noted, 10.00  $\tau$  = TMS;<sup>b</sup>in Hz, E = P or As;<sup>c</sup>unavailable from data;<sup>d</sup>neat;  $J_{13\text{C-H}}$  = 157.8 Hz;<sup>e</sup>ref. 4;<sup>f</sup>probably negative (see text).

TABLE 2

MASS SPECTRUM OF  $\text{ClCH}_2\text{AsH}_2$ 

m/e	rel. abund.	assignment <sup>a</sup>
150	4.4	$\text{As}_2^+$
128	7.4	$^{37}\text{ClCH}_2\text{AsH}_2^+$
127	1.0	$^{37}\text{ClCH}_2\text{AsH}^+$
126	27.6	$^{35}\text{ClCH}_2\text{AsH}_2^+ (23.3), ^{37}\text{ClCH}_2\text{As}^+ (4.3)$
125	4.0	$^{35}\text{ClCH}_2\text{AsH}^+ (2.5), ^{37}\text{ClCHAs}^+ (1.5)$
124	13.3	$^{35}\text{ClCH}_2\text{As}^+ (13.0), ^{37}\text{ClCAs}^+ (0.3)$
123	4.4	$^{35}\text{ClCHAs}^+$
122	1.1	$^{35}\text{ClCAs}^+$
113	5.7	$^{37}\text{ClAsH}^+ (\text{R})$
112	5.0	$^{37}\text{ClAs}^+ (\text{R})$
111	19.8	$^{35}\text{ClAsH}^+ (\text{R})$
110	16.2	$^{35}\text{ClAs}^+ (\text{R})$
92	27.5	$\text{CH}_3\text{AsH}_2^+$
91	8.7	$\text{CH}_2\text{AsH}_2^+$
90	100.0	$\text{CH}_2\text{AsH}^+$
89	62.8	$\text{CH}_2\text{As}^+$
88	55.9	$\text{CHAs}^+ (53.4), \text{CH}_2^{37,37}\text{Cl}_2^+ (2.5)$
87	5.0	$\text{CAs}^+$
86	12.2	$\text{CH}_2^{35,37}\text{Cl}_2^+$
84	28.9	$\text{CH}_2^{35,35}\text{Cl}_2^+$
78	39.8	$\text{AsH}_3^+$

TABLE 2 continued

m/e	rel. abund.	assignment <sup>a</sup>
77	16.2	AsH <sub>2</sub> <sup>+</sup>
76	69.4	AsH <sup>+</sup>
75	33.1	As <sup>+</sup>
51	12.8	<sup>37</sup> ClCH <sub>2</sub> <sup>+</sup>
50	2.6	<sup>37</sup> ClCH <sup>+</sup>
49	43.9	<sup>35</sup> ClCH <sub>2</sub> <sup>+</sup> (38.3), <sup>37</sup> ClC <sup>+</sup> (5.6)
48	7.8	<sup>35</sup> ClCH <sup>+</sup>
47	16.8	<sup>35</sup> ClC <sup>+</sup>
37	2.3	<sup>37</sup> Cl <sup>+</sup>
35	7.1	<sup>35</sup> Cl <sup>+</sup>

<sup>a</sup> Parenthetical numbers are the relative abundances of species of same unit m/e value; (R) represents obvious rearrangement peaks, other fragments may also be the result of rearrangement, e.g., ClCH<sub>2</sub>As; metastable transition data were not available.



TABLE 3

IR SPECTRUM OF  $\text{ClCH}_2\text{AsH}_2$ 

Vib. no.	Assignment	Frequency ( $\text{cm}^{-1}$ )	Intensity <sup>a</sup>
<u>A' Species</u>			
v1	C-H stretching	2950-2970	m
v2	As-H stretching	2085-2130	vs
v3	$\text{CH}_2$ scissors	1410	vw
v4	$\text{CH}_2$ wagging	1188	s
v5	$\text{AsH}_2$ scissors	963	m
v6	$\text{AsH}_2$ wagging	760-800	m
v7	C-Cl stretching	727	m
v8	C-As stretching	528	w
v9	Cl-As-C deformation (not observed)	250 (est.)	-
<u>A'' Species</u>			
v10	C-H stretching	2950-2970	m
v11	As-H stretching	2085-2130	vs
v12	$\text{CH}_2$ twisting	1108	m
v13	$\text{AsH}_2$ rocking	862	m
v14	$\text{AsH}_2$ twisting	760-800	m
v15	$\text{CH}_2$ rocking	700	w-sh

<sup>a</sup><sub>v</sub> = very strong, s = strong, m = medium, w = weak, sh = shoulder.

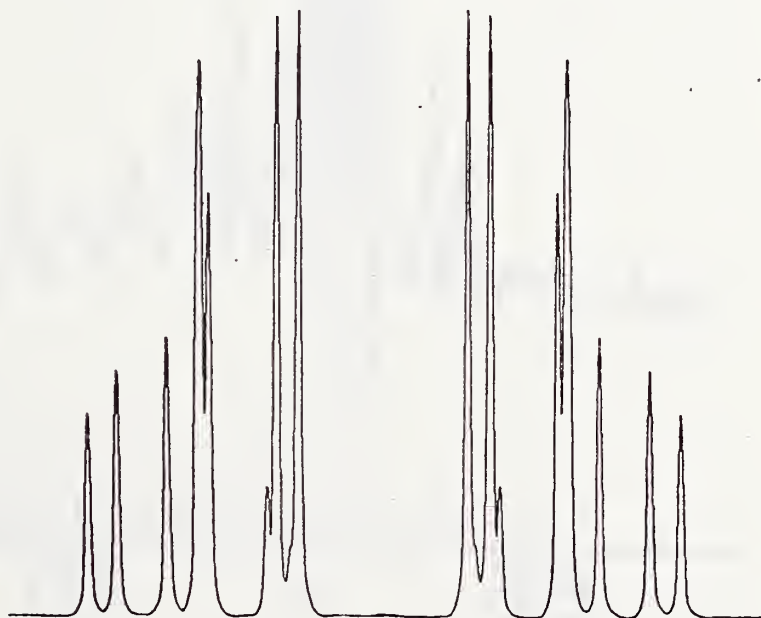
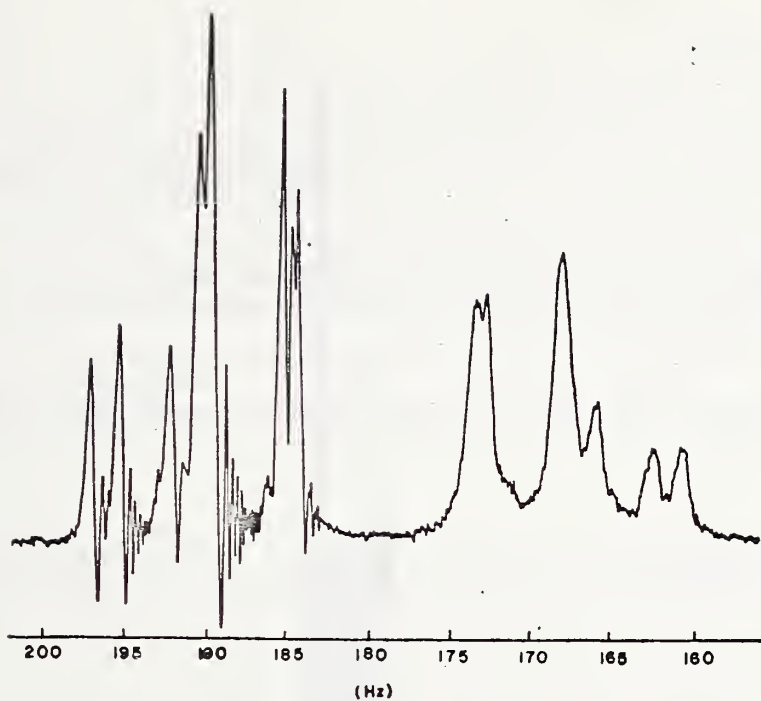


Figure 1. 60MHz pmr spectrum of  $\text{ClCH}_2\text{AsH}_2$  (upper) as a 10% solution in benzene with the "best fit" computer simulation (lower). The up-field half of the observed spectrum is broadened by residual quadrupolar coupling to  $^{75}\text{As}$ . Chemical shifts are measured from TMS = 0Hz.

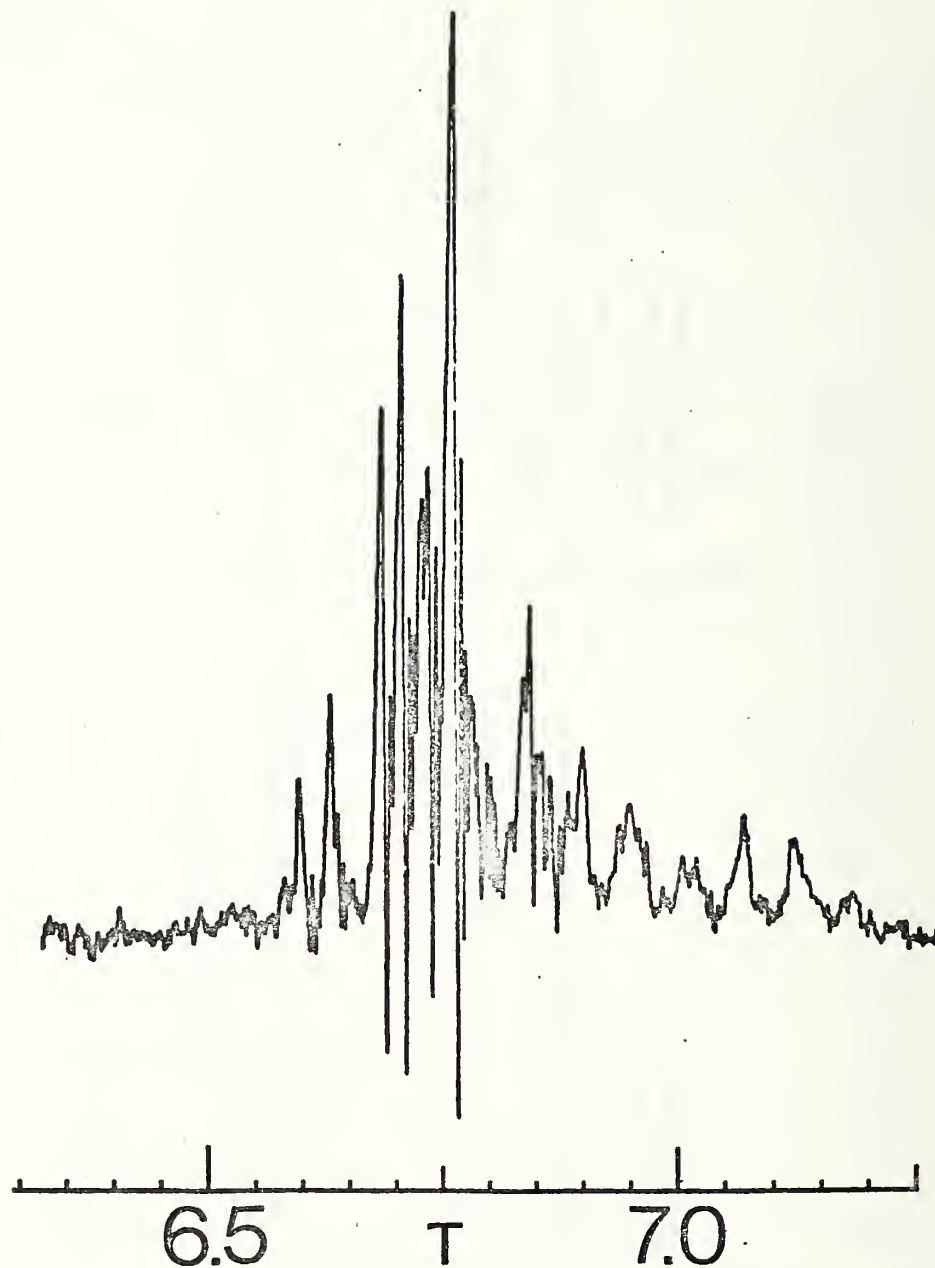


Figure 2. 100MHz pmr spectrum of  $(\text{ClCH}_2)_2\text{AsH}$  as a 10% solution in benzene.  
TMS =  $10\tau$ .

(HALOMETHYL)ARSENIC COMPOUNDS

II.\* PREPARATION AND CHARACTERIZATION OF PENTAKIS(CHLOROMETHYL)CYCLOPENTAARSINE

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## SUMMARY

Hypophosphorous acid reduction of chloromethylarsonic acid produces the novel cyclopolyarsine, pentakis(chloromethyl)cyclopentaarsine (PCCA). PCCA possesses a greater thermal and oxidative stability than other cyclopolyarsines previously studied. The dynamic pmr properties of PCCA are interpreted as a combination of a low-energy limited pseudorotational motion and a higher-energy As-atom inversional process. An alternative to ground-state d-orbital participation in the interpretation of the electronic spectra is offered.

## INTRODUCTION

It was recognized early in the history of organoarsenic chemistry that products containing As-As bonds were common terminations of reactions involving mono- and diorganoarsenic reagents. With diorganoarsenic reagents the terminal products are simple diarsines,  $R_2AsAsR_2$ ; but with monoorgano reagents, the possibility for a great variety of oligomers (usually cyclic) and polymers (chains and ladders) exist, all characterized by the empirical formula  $RA_s$  [1,2]. Cyclic oligomers,  $(RA_s)_n$  where R = alkyl or aryl and  $n = 4$  to 6, all possess puckered rings of As atoms, and especially when R = alkyl, appear to have a single, preferred value of n for each R group. All primary alkyl-substituted cyclopolyarsines are pentamers  $(RA_s)_5$ : R = Me [3], Et [4], Pr [5], *n*-Bu [6], and *i*-Bu [6]; all secondary and tertiary alkyl-substituted cyclopolyarsines are tetramers  $(RA_s)_4$ : R = cyclohex [6], *s*-Br [6], and *t*-Bu [6].  $CF_3$  substitution produces both cyclotetramer and cyclopentamer and is therefore an exception [7,8].



This paper describes the preparation and physical characterization of a new cyclic oligomer, pentakis(chloromethyl)cyclopentaarsine (PCCA),\* of interest because of the presence of both a sterically demanding and electron withdrawing substituent. Nixon reports [9] that one of the products of the decomposition of  $\text{ClCH}_2\text{PF}_2$  under mild conditions is a not well-characterized yellow liquid believed to be a cyclic polyphosphine,  $(\text{ClCH}_2\text{P})_n$ , with n most likely five [10].

#### EXPERIMENTAL

PMCA was prepared by the hypophosphorous acid reduction of sodium methylarsonate [11] but was not distilled before use. Chloromethylarsonic acid, prepared as previously described [12], was reduced in aqueous solution by 50% hypophosphorous acid to the cyclic oligomer,  $(\text{ClCH}_2\text{As})_5$  (PCCA). PCCA separated as an intensely yellow, heavy oil of undetermined boiling point which was purified by repeated 5%  $\text{NaHCO}_3$  and water washings followed by a 2 hr degassing at  $10^{-4}$  mm Hg, but was not distilled. Previous experiences have shown that PMCA undergoes partial, irreversible and not well understood changes on mild heating, e.g., during distillation [4,13]. PCCA is soluble in both benzene and ether, and insoluble in water. (Found: C, 9.72; H, 1.65; Cl, 28.28.  $\text{CH}_2\text{AsCl}$  calcd.: C, 9.66; H, 1.62; Cl, 28.49%)

PCCA's susceptibility to aerobic oxidation is undetectable, as compared to PMCA, which in thin films is pyrophoric. Additionally, no arsine-like

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\*PCCA = pentakis(chloromethyl)cyclopentaarsine,  $(\text{ClCH}_2\text{As})_5$ ; PMCA = pentamethylcyclopentaarsine,  $(\text{CH}_3\text{As})_5$ ; PFCA = pentakis(trifluoromethyl)cyclopentaarsine,  $(\text{CF}_3\text{As})_5$ ; and PECA = pentaethylcyclopentaarsine,  $(\text{CH}_3\text{CH}_2\text{As})_5$ .

odor is found surrounding exposed samples. PMCA often forms solid red-brown modifications on standing which when heated to 180° revert to its original state [13]. Purified PCCA, however, showed no tendency to produce solid forms even after a 20-day exposure to humid air. During its preparation PCCA did form red-brown solids which could not be thermally reverted to a liquid state even when heated to 300° in an evacuated tube.

The product's pentameric state was deduced from its nmr spectrum which according to whether it was measured neat or in solution displayed peaks in integrated ratios of either 2:3 or 2:2:1, and was confirmed by its osmometric molecular weight: found, 589, calcd. 612. Considerable difficulty was experienced in obtaining a satisfactory mass spectrum of PCCA attributable to its extreme involatility. Samples of PCCA heated to 260° under nitrogen showed no evidence of thermal decomposition; PMCA decomposes irreversibly at 205°.

The nmr spectra were recorded on either a Varian A-60D or a Perkin-Elmer R20B each equipped with their manufacturer's variable temperature controller; uv spectra were recorded on a Cary 14.

#### RESULTS AND DISCUSSION

Structural data on pentameric cyclopolyarsines are limited to the methyl derivative. Both electron [3] and x-ray diffraction [13] studies support the presence of a puckered five-membered ring. The absence of symmetry in the crystallographic structure (Fig. 1a) dictates that each methyl group is unique and that, if the solid-state structure persists in solution, the nmr spectrum should consist of five equal-intensity lines. All spectra of cyclopentaarsines show three or fewer lines; even the  $^{19}\text{F}$  nmr spectrum of

PFCA, where chemical shift differences are large and the likelihood of accidental degeneracies small, displays only a three-line pattern of intensity ratio 2:2:1 [14]. Furthermore, five-line spectra have not been observed for either PMCA or PFCA even when cooled to  $-100^{\circ}$  [14]. For PCCA, depending upon solvent, dilution, and temperature, spectra always show either a 2:2:1 or 2:3 pattern.

One is forced, therefore, to propose a fluxional motion for cyclopentaarsines which generates a time-average plane of symmetry (Fig. 1b). As the symmetry generating motion is still rapid at very low temperatures, it must be characterized by a low activation free energy. The phenomenon responsible for these effects is likely one of five possibilities: 1) As atom inversion, 2) ring opening-closing equilibria in which pentameric forms are retained, 3) ring opening-closing equilibria involving alteration in oligomer size, 4) pseudorotation, and 5) that the asymmetrical solid-state structure results from crystal packing requirements which relax in solution (a non-fluxional interpretation).

Although Lambert has shown that simultaneous inversion of both As atoms in diarsines is more rapid than single inversion in monoarsines (due perhaps to the stabilization of planar intermediates through a maximization of  $p\pi - d\pi$  interactions) [15], reasonable estimates for minimal activation barriers for As-atom inversion are undoubtedly not less than  $80-85 \text{ kJmol}^{-1}$  [16], a barrier seemingly unsurmountable at  $-100^{\circ}$  especially since a symmetry-generating motion would be expected to have a negative activation entropy.  $\Delta G^{\ddagger}(-100^{\circ})$  for the observed symmetry generating motion can be approximated from chemical shift data as being not greater than  $25-30 \text{ kJmol}^{-1}$ . In view of this, a

recently proposed wag-inversion mechanism [14] must be viewed with skepticism. Furthermore, Mislow has also demonstrated that inversion barriers in phosphines (including diphosphines) can be correlated with substituent electronegativities: the greater the electronegativity the higher the barrier [16,17]. Inversional processes may, however, be responsible for a different, high-temperature fluxional behavior described below.

All ring opening-closing equilibria necessitate As-As bond cleavage, but may be facilitated by impurities introduced either during preparation or through thermolytic or photolytic decomposition of pure cyclopolyarsine. Examples of sample-history dependent phenomena are known [4]. Again, however, although possibly relevant at elevated temperatures, ring opening equilibria whether catalyzed or not, require not only the expenditure of the As-As bond dissociation energy (ca. 150 kJmol<sup>-1</sup>), but also the loss of the difficulty estimated stabilization achieved through transannular, non-bonded As-As interactions.\*

Most attractive of the alternatives appears to be pseudorotation, a rotation of the position of maximum puckering in stepwise, random, or alternate exchange (between two favored positions) patterns resolvable into vertical motions of As atoms. Pseudorotation of unspecified pattern was first suggested by West [4] as an explanation for these low-energy fluxional processes.\*\*

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\*It is difficult to account for the remarkable thermal stability of cyclopolyarsines compared to catenapolyarsines unless additional sources of stabilization, e.g., transannular attractive interactions, are proposed.

\*\*Wells [14] has proposed that the high-energy phenomena described elsewhere in this paper are attributable to a stepwise pseudorotation.

Unlike inversion, pseudorotation preserves the non-equivalency of As atoms. Differences must therefore exist in the barriers for specific pseudorotational transitions (both 1,2 and 1,3 exchanges are possible). One concludes that pseudorotation need not occur at all As atoms with equal frequency, i.e., the differences between the bottoms and saddle points on a five-well, free-energy annulus will differ at each position. The simplest (and therefore probably least energy) pseudorotational motion capable of generating the required symmetry would be one that made the (1) and (2) positions equivalent and transferred the puckered position to (4) (see Fig. 1) followed by a return of puckering to either position (1) or (2). Note that motion at position (4) is not a requirement; a simple torsional motion along the As(1)-As(2) axis suffices.

The general features of the solid-state structure of PMCA also pertain to those cyclopentaphosphines whose structures have been determined [18]. It is reasonable, therefore, to conclude that the favored ring conformation in solution phases closely resembles the solid-state structure, a structure preferred for its minimization of repulsive electronic and steric interactions and not the result of crystal packing requirements.

The pmr spectrum of PCCA would be expected to be more complex than that of PMCA. In the absence of a symmetry generating motion, not only are the chloromethyl groups anisochronous, but so also are the two protons of each group, producing (in theory) five, distinct AB spin patterns (presuming that coupling between adjacent chloromethyl groups is negligibly small). In the presence of the proposed symmetry-generating torsional motion, the spectrum would reduce to two distinct AB patterns (the protons on C(1) and C(2) producing degenerate AB patterns, likewise C(3) and C(5)) and a single line



for the isochronous protons on C(4). As  $J(AB)/\Delta\nu(AB)$  becomes large ( $>1.0$ ), the appearance of an AB pattern collapses to a closely-spaced central doublet as the outer lines fade in intensity, and as  $\Delta\nu(AB)$  approaches zero, all lines collapse to a singlet. It is reasonable to expect that the values of  $\nu(A)$  and  $\nu(B)$  will differ only slightly.

As a 20% (by weight) solution in chlorobenzene, PCCA shows a narrow line-width ( $< 1.0\text{Hz}$  at half height) three-line spectra in a 2:2:1 intensity ratio at 5.91, 6.05 and 6.06  $\tau$ . The two closely spaced high field peaks merge at similar dilution in benzene and toluene. Since the line with a relative intensity of one must represent the  $\text{ClCH}_2$  group on As(4) and since the  $\text{ClCH}_2$  environments for positions (3) and (5) resemble (4) more than (1) or (2), the 5.91 $\tau$  line is assigned to the (1),(2) pair and the 6.05 $\tau$  line to the (3),(5) pair.

At room temperature and below, spectra of neat PCCA are badly viscosity broadened as seen also in PMCA, but at 42° show the same three-line spectrum found in chlorobenzene. (Fig. 2) Two smaller peaks (totaling about 10% of the intensity of the main peaks) appear upfield at 6.22 and 6.27 $\tau$ . The presence, position and intensity of the weaker peaks are not a function of sample history or its method of preparation, and must therefore, be due to species derived from, and in equilibrium with, PCCA. Similar weak up-field peaks are found in neat samples of PMCA and similar arguments have been applied to their origin [4,14,19].

The nmr spectra of PCCA lead, therefore, to the conclusion that the chemical shift difference between geminal protons at positions (1), (2), (3) and (5) must be unobservably small, i.e., the anticipated AB quartet patterns have collapsed to singlets. A 100 MHz nmr spectrum of PECA has

been published by West [4]. At 120° where all viscosity broadening has disappeared, he finds a spectrum of high complexity, deriving, he suggests, from slow pseudorotation producing non-equivalency among all ethyl groups. If West's suggestion is accepted, the conclusion must be that PMCA pseudo-rotates nmr rapidly at -100° while PECA does so only slowly at +120°; a 220° temperature difference for these essentially isoentropic processes appears unreasonable. Clearly, however, the methylene portion of the ethyl group should, at least in theory, also contain anisochronous protons and produce, in the presence of nmr-fast pseudorotation, one A<sub>2</sub>B<sub>3</sub> and two ABC<sub>3</sub> patterns (which could be indistinguishable from A<sub>2</sub>B<sub>3</sub> patterns if  $\Delta\nu(\text{AB})$  is small). In fact, West's spectrum looks more like overlapping A<sub>2</sub>B<sub>3</sub> patterns where  $J(\text{AB})/\Delta\nu(\text{AB})$  is about 0.1; the anticipated geminal constant for a freely rotating ethyl group is about 7Hz and the PECA spectrum appears to have a  $\Delta\nu$  of about 75Hz. Thus if, as in PCCA, the chemical shift difference between geminal (CH<sub>2</sub>) protons is unobservably small, West's spectrum is reasonable for three overlapping A<sub>2</sub>B<sub>3</sub> patterns, not five triplet-quartet (first-order ethyl) patterns.

When PMCA is heated above 160° complex, often poorly reproducible, and sometimes sample history dependent phenomena occur [4]. Wells [14] reports that the nmr multiline spectra of PMCA and PFCA collapse reversibly to single lines; above about 170° the lines broaden again continuously to the highest temperature observed, 200°. In the range of 170-200° the smaller upfield lines also broaden and eventually disappear. West, however, finds no loss of triplet structure or alteration in the upfield peaks when fresh samples of PMCA are heated to 178°, but does find the previously reported broadening and

collapse of all lines when samples have been preheated at 190° for 2 hrs [4]. He found that preheated samples of PMCA contained a high mass spectral abundance of  $(\text{CH}_3)_4\text{As}_2^+$  ions at m/e 210 that were absent in unheated samples. Tetramethyldiarsine is a product of the pyrolysis of  $(\text{CH}_3\text{As})_5$  and does catalyze further ring opening; ring opening/closing equilibria are possible explanations for the high temperature nmr phenomena [19].

Our own experience with PMCA resembles that of Wells [14]; although no m/e 210 ions were found in our samples, coalescence was achieved at about the same temperature he observed. Samples of PMCA that were thoroughly degassed or left undegassed, samples purposely poorly washed to leave residues of excess hypophosphorous acid or carefully and repeatedly washed, samples distilled or crude, all showed coalescence at  $\pm 3^\circ$  of Wells' temperature.\* The exposure to normal laboratory fluorescent illumination did, however, produce significant changes; after one week, exposed samples of highly refined PMCA showed a coalescence temperature 10° below Wells' temperature. West does not report if his preheating occurred in light or darkness.

Up to 80° the three-line neat PCCA spectrum sharpens as viscosity effects lessen. Above 80° the lines again broaden; the two closely spaced lines at 6.05 and 6.05 $\tau$  coalesce at 110° (presumably the result of line broadening or line position changes but not chemical averaging) and both remaining lines continue to broaden but do not coalesce up to 160° where heating was discontinued (Fig. 2). If extrapolated, the broadening trend would lead to coalescence at about 185°, very near the coalescence temperature for PMCA.

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\*Unrefined samples did show much more rapid formation of polymeric red-brown catena-polymethylpolyarsine than found in refined samples.

Contrary to the observations for PMCA [4,14], however, high-temperature behavior of PCCA is not rapidly reversible; the broadened, two-line spectrum of neat PCCA at 160° does not fully revert to its room-temperature spectrum until 24 to 30 hrs have elapsed. Since all other cyclopentaarsines so far studied rapidly (as fast as samples can be cooled in the spectrometer, ~ 20°/min) equilibrate on cooling, only the steric bulk of the ClCH<sub>2</sub> groups in PCCA can account for the retarded rates of reequilibration. At these elevated temperatures, As-atom inversional barriers for PCCA can be realistically surmounted. In this regard, Lambert has found that As-atom inversion in diarsines becomes nmr-rapid at about 180° [15]; at 180° coalescence of the methyl resonances for the d,l and meso forms of 1,2-dimethyl,1,2-diphenyl-diarsine is achieved through inversion (coupled with As-As bond rotation).\*

For cyclopentaarsine initially in the crystallographic structure, inversion at three of the five As atoms produces structures possessing up/down non-bonding electron pair (or substituent) arrangements different from that of Fig. 1 as suggested by Van Wazer [19]. In Fig. 3 the various possibilities are shown. The structures have been arranged intuitively in order of increasing internal energy by consideration of the number of nearest-neighbor electron-pair, electron-pair repulsions. We propose that these higher energy invertomeric forms become significantly populated at higher temperatures producing line broadening. On cooling, PMCA rapidly reverts to its thermal ground state, but PCCA is apparently "frozen out" in thermally excited invertomeric forms, i.e., PCCA readily supercools. The higher barrier to interconversion of invertomeric forms for PCCA must derive from crowding imposed by the

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\*Mislow [16] suggests that the coalescence process may be intermolecular. This suggestion has received recent support from a restudy [20] of dynamic processes in diphosphines.

sterically demanding chlorine atom. Each inversion requires a simultaneous C-As bond rotation to sterically accommodate the Cl atom (convincingly seen from space-filling models), but such rotations are restricted by the severe interaction of the Cl atom with the As atoms three bonds removed. These steric entanglements prevent rapid return to a thermal ground state. Concentration dependency studies in t-butyl-benzene indicate that the rate of return to ground state is an intramolecular process. There is no reason to believe that the population of excited-state invertomeric forms does not also satisfactorily explain the high-temperature behavior for all cyclopentarsines.

PCCA exhibits several other properties that differentiate it from other cycloarsines. It is, for instance, indefinitely stable in contact with humid air, whereas PMCA is pyrophoric, and PFCA is rapidly hydrolyzed at room temperature [7]. Consistent with its stability to oxidation and hydrolysis is our finding that PCCA possesses the longest wavelength uv absorption of any cycloarsine reported,  $\lambda(\text{max})$  350nm, as compared to 300nm for PMCA when measured as  $10^{-3}\text{M}$  solutions in benzene. This uv transition is attributed by many to a lone-pair delocalization into an empty d level or other orbital of suitable symmetry on an adjacent arsenic atom [21]. There is great difficulty, however, in extending this argument to a picture of circumannular delocalization in the classical aromatic sense. A molecular orbital constructed from p and d orbitals cannot produce conjugation in a non-planar structure via  $p\pi - d\pi$  bonding.

An alternative to ground-state d-orbital involvement can be proposed. Two filled molecular orbitals constructed of s and p atomic orbitals, e.g., two non-bonding electron pairs on adjacent As atoms, can interact to an extent determined by their dihedral angle (along the As-As bond axis) reaching a



maximum at an angle of 0°. Although the total energy of such a system remains constant with variation in dihedral angle (if secondary effects are neglected), the HOMO [23] does increase in energy thus lowering the HOMO-LUMO separation, Fig. 4. Similar molecular-orbital descriptions have been used effectively by Weiss [22] in the analysis of charge-transfer spectra of disulfides and by Cowley and Dewar [23] in a photoelectron-spectroscopy study of CF<sub>3</sub>-substituted cyclotetra- and cyclopentaphosphines. Cowley and Dewar find evidence not only for 1,2 lone-pair interaction but also for transannular interaction.\* Other aspects of their data strongly support the position that  $p\pi - d\pi$  bonding is relatively unimportant in phosphorus-phosphorus bonding; one can safely assume the extendibility of these results to arsenic-arsenic bonding as well. If, by analogy to cyclopolsilanes [24,25], the LUMO for cyclopolyarsines is largely  $d$  in character, some excited state delocalization appears likely.

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\*It should be pointed out that in their study Cowley and Dewar [23] found evidence for lone-pair interactions in (CF<sub>3</sub>P)<sub>4</sub> but not (CF<sub>3</sub>P)<sub>5</sub>. This they attribute to the absence of symmetry in the pentamer but give reference only to a solid-state structural determination. In solution, however, Wells [14] has found, as is true also for other cyclopentamers, that at least  $C_s$  symmetry is achieved permitting symmetry-allowed lone-pair orbital interactions. This leads to three presently unresolvable interpretations: 1) cyclopentamers revert to an asymmetric structure in the vapor state (required for photoelectron spectroscopy), 2) fluxional motions which create the  $C_s$  symmetry prevent orbital association (unlikely considering the vast difference in time scales), and 3) that Cowley and Dewar's interpretation of their spectra is incorrect.

It is important to note that the lowest energy absorption in cyclopentarsines (and phosphines) is considerably red-shifted compared to either cyclotetra- or cyclohexarsines [21,26], and that it is only the cyclopentamers that require a time-average structure with a  $0^\circ$  (or near  $0^\circ$ ) dihedral angle between two adjacent lone-pairs.

The steric restrictions imposed by the  $\text{ClCH}_2$  groups may have a dampening effect on pseudorotation (or a limited pseudorotation such as the torsional motion earlier described) thus restraining the oscillations to a narrower region either side of a  $0^\circ$  dihedral angle.

In bis [catena-poly(methylarsenic)] (BCPA), a high-molecular-weight ladder polymer constructed of  $\text{CH}_3$ -substituted As atoms [2], all non-bonding electron pairs along a ladder upright are constrained to a nearly  $0^\circ$  dihedral angle relationship. BCPA is intensely purple,  $\lambda(\text{max})$  ca. 450nm and shows the electrical properties of an intrinsic semiconductor with an energy gap of about 1.3 eV. Ac conductivity measurements strongly indicate a "hopping" mechanism for electron mobility [27] suggesting that extended excited-state delocalization in this (and perhaps all) polyarsines is unimportant in confirmation of West's electrochemical results [24].

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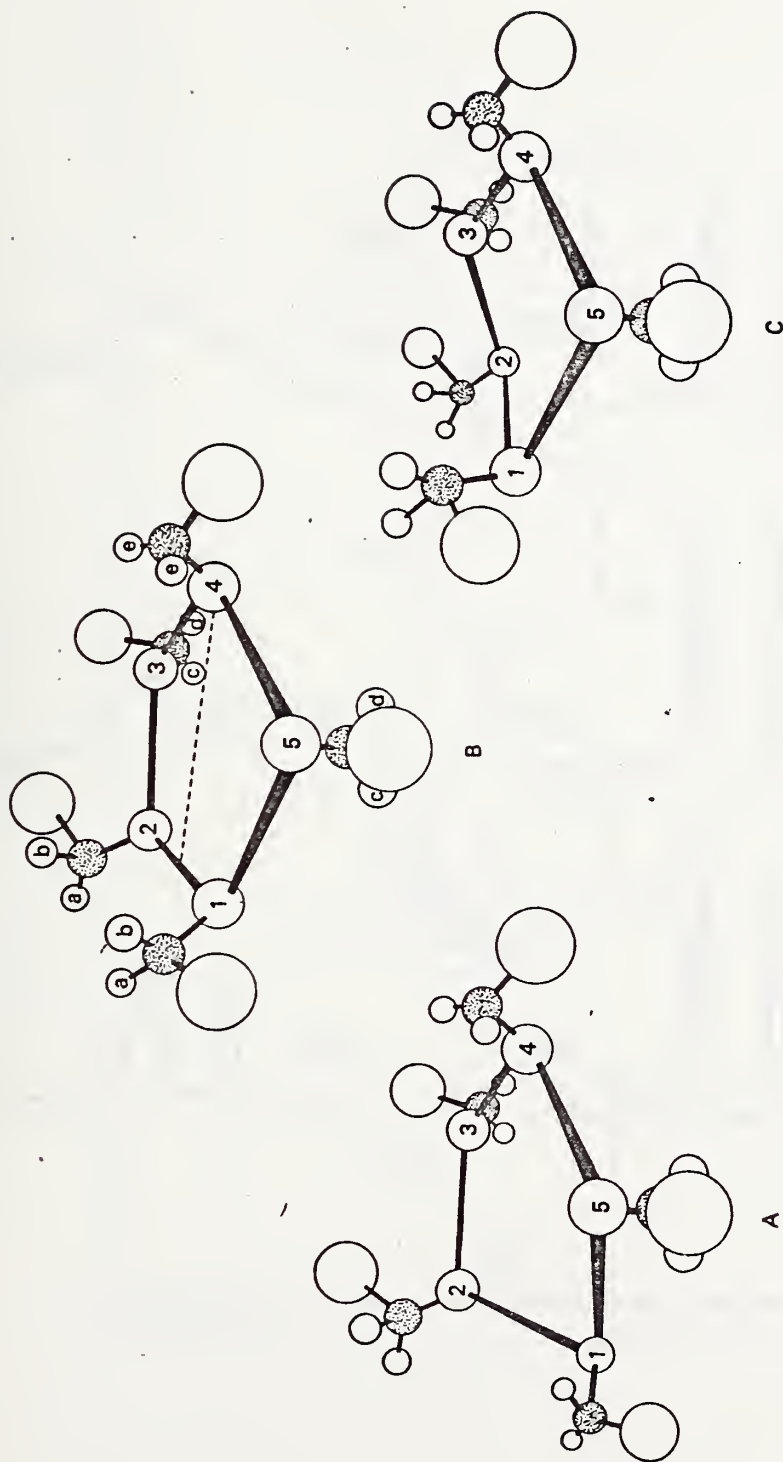


Figure 1. A schematic depiction of a torsional (restricted pseudorotational) motion of  $(\text{ClCH}_2\text{As})_5$  along the  $\text{As}(1) - \text{As}(2)$  bond which converts structure A into its mirror image, structure C, through the symmetrical intermediate, structure B (--- represents the intersection of a vertical plane of symmetry). Structures A and C derive from the crystallographic structure of  $(\text{CH}_3\text{As})_5$  (ref. 3). The lower case letters in structure B designate isochronous pairs of protons.



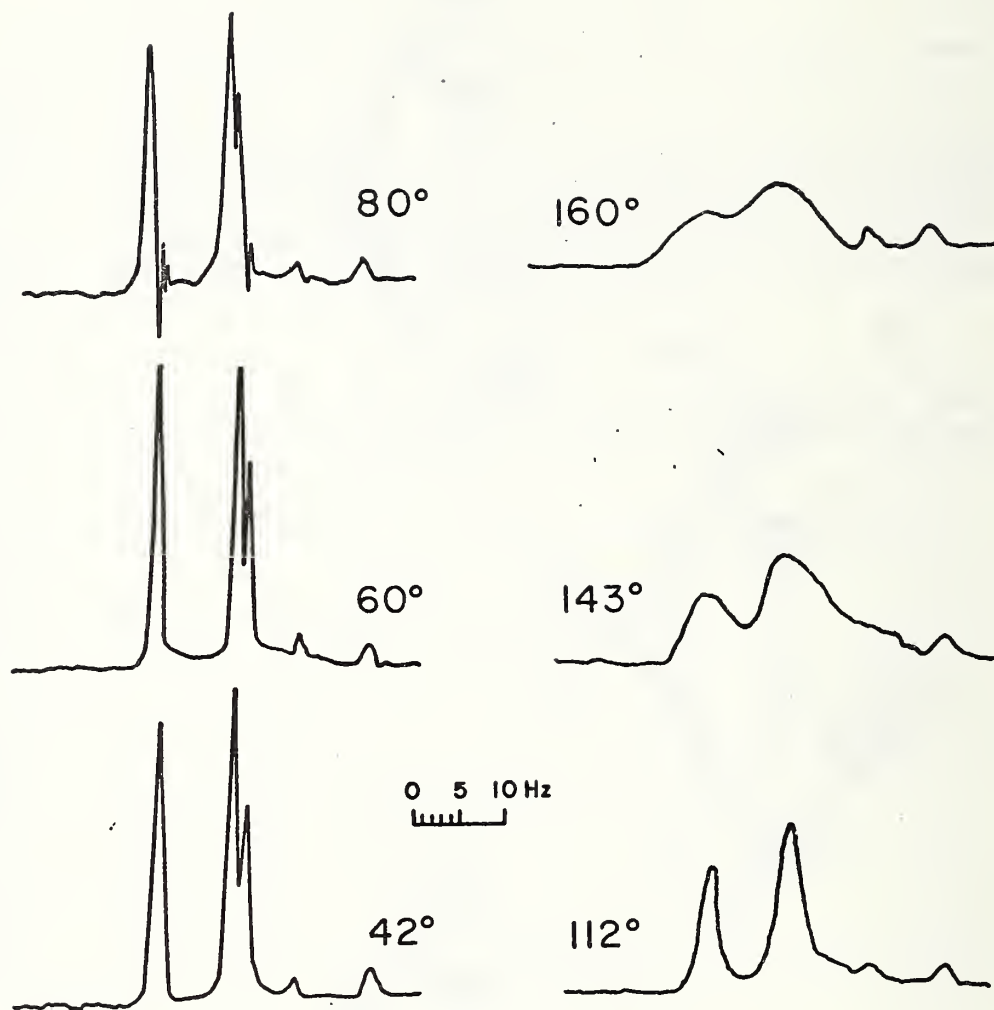


Figure 2. Variable-temperature 60MHz spectra of  $(\text{ClCH}_2\text{As})_5$ .

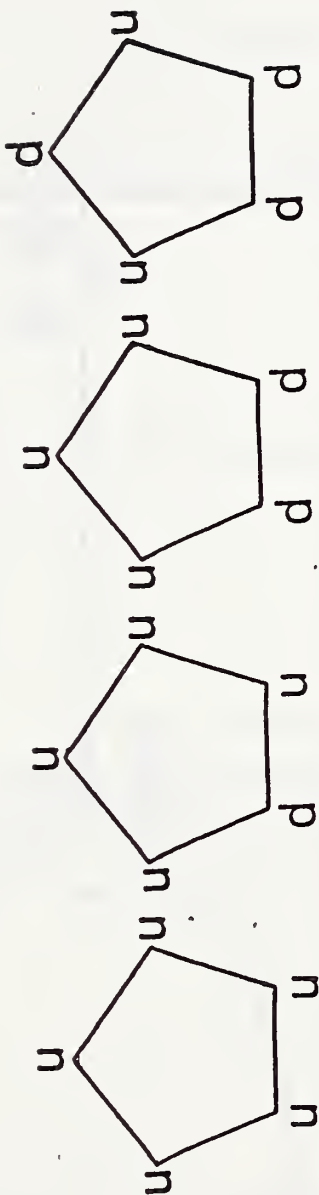


Figure 3. Four possible inversive isomers for a five-membered ring of arsenic atoms based upon the up("u")-down("d") relationship of non-bonding pairs (or substituents). The isomers are intuitively arranged in order of decreasing internal energy (from left to right) by consideration of non-bonding pair interactions.

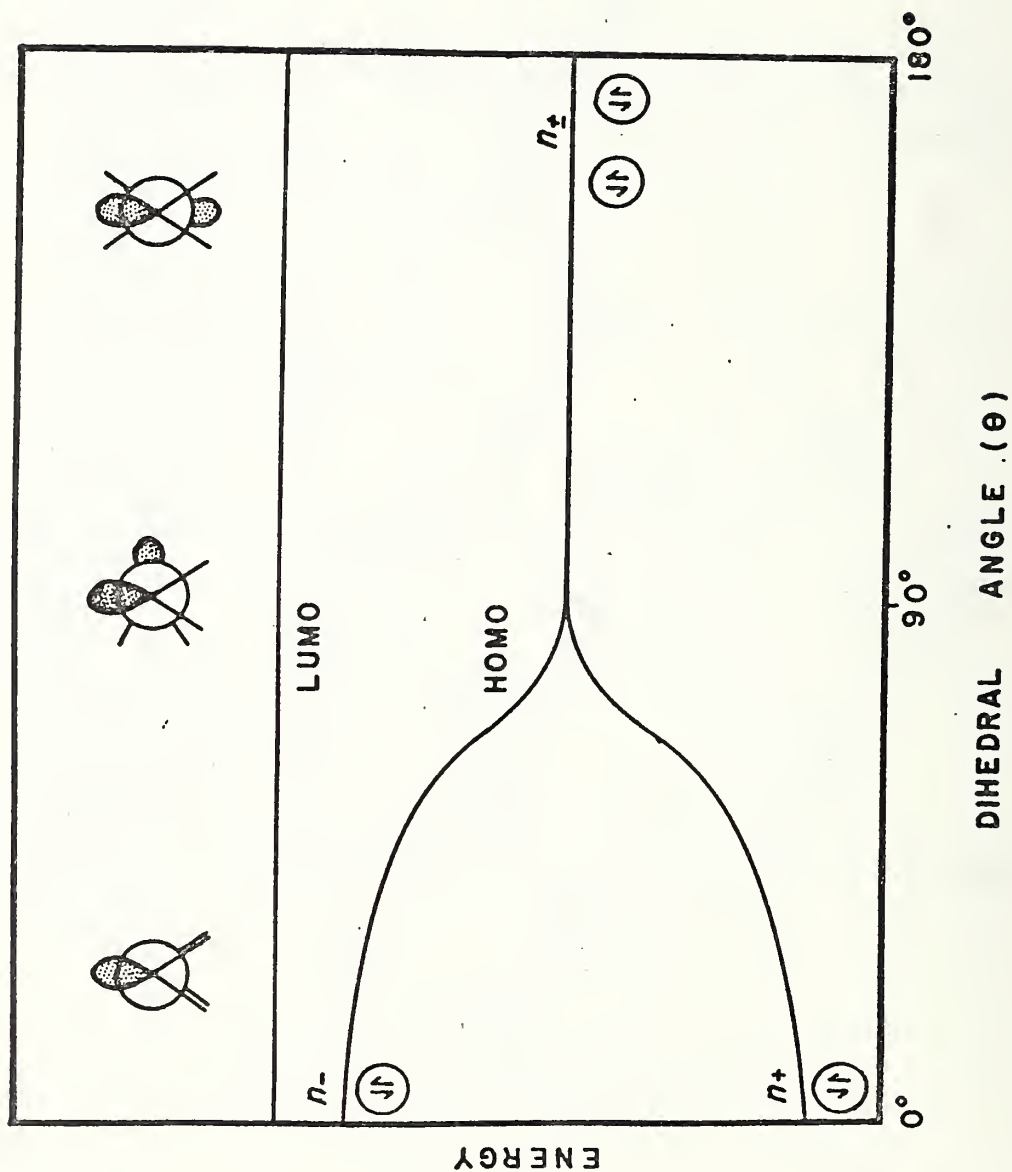


Figure 4. The variation of the HOMO-LUMO separation as a function of the dihedral angle ( $\theta$ ) relating non-bonding pairs on adjacent arsenic atoms. The interaction of electron pairs, while a  $\cos(\theta)$  function of the dihedral angle, need not fall to zero at  $90^\circ$ .

A REPORT SUBMITTED  
TO  
NATIONAL BUREAU OF STANDARDS

TO  
DR. MARTIN BROADHURST

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SYNTHESIS OF POLY(ARYLAMINOPHOSPHAZENES)

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## SYNOPSIS

The synthesis of a series of poly[bis(arylamino)phosphazenes] is described. The polymers usually were prepared by treatment of polydichlorophosphazene in benzene-tetrahydrofuran with arylamines/triethylamine at reflux for 48-144 hr. The polymers, having viscosities of 0.3 - 1.4 dl/g, are essentially free of active chlorine sites, as shown by elemental analysis and their long-term hydrolytic stability. Thermal analyses revealed glass transition temperatures between 53° and 105°C and decomposition temperatures between 243° and 266°C. Analysis by differential scanning calorimetry revealed no first order endothermic transitions. For comparison with the arylamino polymers, poly(diethylaminophenylaminophosphazene), poly[bis(benzylamino)phosphazene], and poly[bis(g-phenethylamino)-phosphazene] were prepared and are described.

## INTRODUCTION

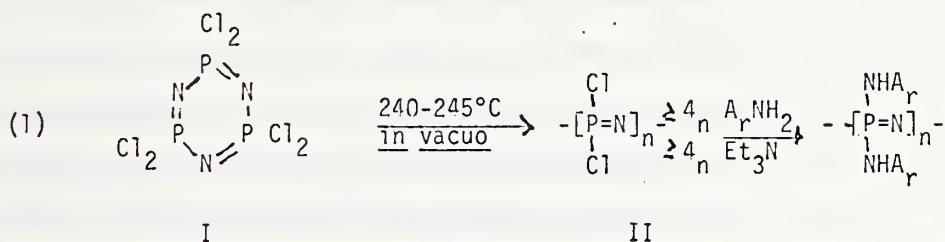
The high-temperature melt polymerization of hexachlorocyclotriphosphazene (I) is known to lead to high molecular weight, open-chain polydichlorophosphazene (II).<sup>1,2a,3</sup> The hydrolytically unstable elastomer II may be converted to hydrolytically stable derivatives by nucleophilic replacement of the active chloro ligands with organo groups.<sup>2a</sup> The properties of the resulting polymers depend greatly on the nucleophile chosen, a fact which allows polydichlorophosphazene to act as a common precursor to a large variety of materials.

Although a large number of poly(aryloxy-),<sup>3</sup> poly(alkoxy-)<sup>2a</sup> and poly(alkylaminophosphazenes)<sup>4,5</sup> have been prepared, only scant attention has been paid to the synthesis of poly(arylamino phosphazenes)(III). While there are numerous reports describing the reactions of cyclic trimer I and octachlorocyclotetraphosphazene with various arylamines,<sup>2b</sup> poly[bis(phenylamino)phosphazene] (IIIa) appears to be the only example of the polymeric class III that has been prepared.<sup>4</sup> Because of the paucity of information regarding arylamino derivatives of II, and because of our continuing general interest in the chemistry of polyphosphazenes<sup>3,6</sup> and their potential applications,<sup>7</sup> we undertook the synthesis of a series of poly(arylamino phosphazenes).

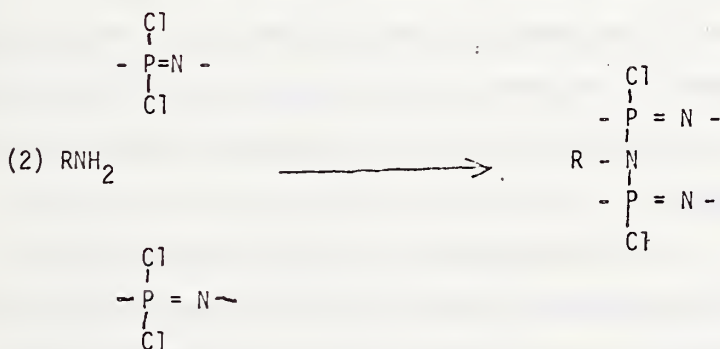
## RESULTS AND DISCUSSION

Cyclic trimer I was polymerized as described previously,<sup>3</sup> and polydichlorophosphazene (II) was isolated in yields of 17 to 43% (eq. 1).

Although the reaction of polymer II with



ammonia and methylamine above room temperature can lead to cross-linked products (eq. 2),<sup>4,5</sup> anilines react cleanly with II to give soluble products (eq. 1), presumably because steric constraints prohibit the cross-linking reaction.



In the synthesis of poly(alkylaminophosphazenes), both excess alkylamine or a tertiary amine have been employed as hydrohalide acceptors.<sup>5</sup> We found the use of the latter to be more satisfactory, and the poly(arylaminophosphazenes) (III) reported here usually were prepared by the treatment of polymer II in tetrahydrofuran-benzene with arylamine/triethylamine (both amines usually were in 4 to 5-fold molar excess) at reflux temperatures (eq. 1). Poly[bis(phenylamino)phosphazene] (IIIa), prepared using triethylamine as the HCl acceptor, has a higher intrinsic viscosity and less residual chlorine than IIIa prepared using aniline alone, if all other reaction conditions remain equal. Aniline, when added dropwise to a solution of II, appears to react rather slowly at room temperature, aniline hydrochloride appearing only after heating has commenced. On the other hand, dropwise addition of a solution of aniline and triethylamine to II results in almost immediate formation of precipitate (triethylamine hydrochloride), and the reaction is quite exothermic. Also, the formation of polymer hydrochloride salt during the reaction of II with alkylamines has been reported, and prolonged treatment of the product with a tertiary amine was required to remove traces of HCl,<sup>4</sup> a problem that should be circumvented by the use of triethylamine as the HCl acceptor during reaction.

The reactions of aniline, m- and p- alkyl-, and p-methoxyphenylamine with polydichlorophosphazene are essentially complete after 48-56 hr at reflux (products IIIa-g), with yields of purified products ranging from 25% to 73% (Table I). Difficulties were encountered during the synthesis of poly[bis-(m-methoxyphenylamino)phosphazene], which was isolated in pure form in about 5% yield. Also, steric hindrance prohibits complete

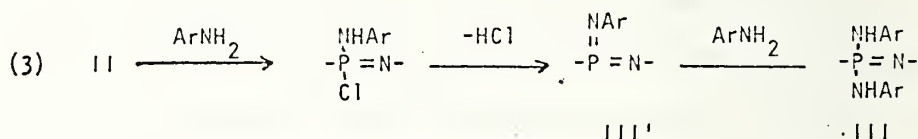
reaction of o-toluidine with II under the conditions discussed above, since the product can cross-link due to attack of water (used in purification) on the labile P-Cl bonds<sup>2c</sup> remaining on the polymer chain. Thus, the material gave only a gel when dissolution in common solvents was attempted. This insoluble material contained 4.85% residual chlorine.

In general, preparations of poly[bis(halophenylamino)phosphazenes] (IIIh-k) required longer reaction times (up to 144 hr.) compared with the syntheses of IIIa-g, probably owing to lesser nucleophilicity of the halophenylamines. Yields of the halophenylamino polymers ranged from 22% to 62% (Table I), with the exception of IIIh, which was isolated in 3% yield. Use of higher boiling solvents (diglyme-toluene) to decrease reaction times resulted in extensive degradation of the polymer backbone. The reaction of m-aminobenzotrifluoride with polymer II gave a substituted product in reasonable yield (21%) but with a low inherent viscosity (0.12 dl/g) and a poor fluorine analysis.

All of the arylamino polymers listed in Table I contain less than 1% residual chlorine, presumably as P-Cl, except for IIIk (1.09%) and the chlorophenylamino polymers IIIh and IIIi, for which no direct measurement of small amounts of P-Cl is available. Carbon analyses for those arylamino polymers shown in Table I were from 0.90% to 3.19% below theory and have no correlation with the amount of residual chlorine present. Similar behavior has been observed for certain poly(alkylaminophosphazenes) and was ascribed to the presence of impurities.<sup>4</sup> That substitution of chloro ligands is virtually complete is demonstrated not only by the low chlorine content of polymers III, but also by the fact that they apparently are stable and remain soluble indefinitely,

a strong indication that the number of labile P-Cl bonds remaining in the polymer is small. For example, polymers IIIa, IIIc, and IIIg, which had intrinsic viscosities of 1.4, 1.4, and 1.3 dl/g respectively immediately after isolation, showed only slight decreases in viscosity (1.2, 1.02, and 1.2 dl/g respectively) after storage under ambient laboratory conditions for almost a year.

Although the slightly low carbon analyses for III possibly are due to the presence of trace impurities<sup>4</sup> or incomplete burning of III during analyses, they may reflect structural variations in the polymer chain. One possible variation could be the imino intermediate (III') shown in eq. 3. After initial substitution of a unit of II by



an arylamine molecule, the imino group might be formed by elimination of HCl, as shown. Addition of a second arylamine molecule to III' would give structure III. Survival of a few imino groups could account for the low carbon analyses, and the fact that triethylamine as a hydrohalide acceptor gives IIIa with less residual chlorine than when aniline, a weaker base, is used in excess lends some support to this explanation for the analyses of the arylamino polymers. Also, formation of imino intermediates during the reactions of trimer I with ammonia<sup>9</sup> and with tert-butylamine<sup>10</sup> has been proposed. However, treatment of polydichloro-



phosphazene (II) with a 20-fold molar excess of aniline or with a 10-fold molar excess of aniline and a 10-fold molar excess of triethylamine yields products for which the carbon analyses are about 2% below theory; it seems unlikely that the imino structure III' would survive such large excesses of reactants. In addition, one would expect that any imino groups that survive the reaction would be at least as labile to attack by water (used in purification) as would P-Cl and therefore provide a cross-linking site just as effective as P-Cl. Such cross-linking, as mentioned, is not observed for the arylamino polymers. Even so, a small number of imino groups, as well as other structural variations, would be difficult to detect and cannot be ruled out completely.

The glass transition temperatures (DSC) of polymers III are rather high (53° to 105°C; Table I) compared with those of poly(aryloxyphosphazenes) (-37° to 6°C<sup>3</sup>). A similar difference exists between poly(alkoxyphosphazenes) (-84° to 14°C<sup>2d</sup>) and poly(alkylaminophosphazenes) (-11° to 30°C<sup>4,5</sup>), suggesting lower torsional mobility of the amino compared with the oxy analogs.<sup>5</sup> Hydrogen bonding has been suggested as a reason for this decrease in torsional mobility,<sup>10</sup> although the glass transition temperatures of poly[bis(piperidino)phosphazene] (19°C<sup>4</sup>) and poly[bis(dimethylamino)phosphazene] (-4°C<sup>4</sup>), polymers in which there is no opportunity for hydrogen bonding, are in the range of those of primary alkylamino polymers. The presence of aryl groups in III also contributes to their high glass transition temperatures, since the glass transitions of poly(aryloxyphosphazenes) occur at much higher temperatures than those of the alkoxy polymers. Solution cast films of some of the arylamino polymers are quite brittle, as one would expect

for materials having such high glass transition temperatures.

Polymers III gave no indication of having simple first order endothermic melting points (DSC).

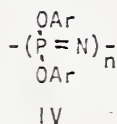
The decomposition temperatures of the poly(arylamino-phosphazenes) range from 243° to 266°C (TGA) in static air (Table I) and are generally lower than those of the poly(aryloxyphosphazenes) measured under oxygen (250° to 400°C<sup>3</sup>). The TGA curve of poly[bis(p-methylphenylamino)phosphazene] (IIIb), which is typical for polymers III, is shown in Figure 1 (curve A). The TGA curves of poly[bis(trifluoroethoxy)phosphazene] (curve B) and poly[bis(p-methylphenoxy)phosphazene] (curve C) also are shown. A noteworthy feature of Figure 1 is that IIIb, like its aryloxy analog, retains appreciable residue at 700°C in contrast to the trifluoroethoxy polymer, which is completely pyrolyzed at 500°C. For the arylamino polymers III, 13-35% of their original weight remains at 700°C.

Characteristic infrared absorption, due to PN stretch, occurs at  $\sim 1200\text{ cm}^{-1}$  (Table I) for the poly(arylamino-phosphazenes). Absorption of PN at  $\sim 930\text{ cm}^{-1}$ ,<sup>4</sup> (Table I) also was observed, as was the NH stretching frequency at  $\sim 3400\text{ cm}^{-1}$ .

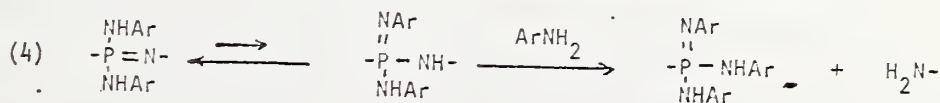
Proton nmr spectra of polymers III are, as expected, poorly resolved (room temperature), but are consistent with the assigned structures.

The solubility characteristics of IIIa-g differ somewhat from those of IIIh-k. All of the polymers are soluble in tetrahydrofuran and benzene, and IIIa-g are soluble in chloroform but insoluble in methanol. The reverse is true for IIIh-k, which are quite soluble in methanol, but insoluble in chloroform.

Intrinsic viscosities were obtained for polymers IIIa-g and are shown in Table I. Curiously, poly[bis(halophenylamino)phosphazenes] (IIIh-k) were found to give anomolous viscosity behavior, and thus only inherent viscosities were measured (Table I). It is interesting to note that the viscosities of polymers III are in many cases significantly lower than those of poly(aryloxyphosphazenes) (IV) reported earlier, which ranged from 1.6 to 3.2 dl/g.<sup>3</sup> These data probably reflect greater degradation of the P-N backbone during aminolysis of



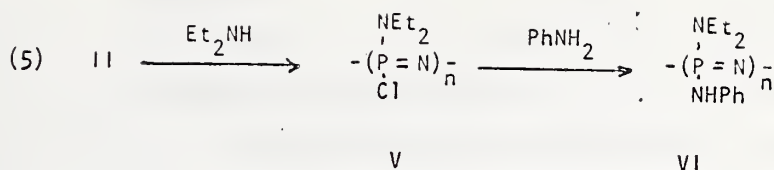
polydichlorophosphazene (II) than occurs when II is treated with aryloxides, although reaction conditions of the latter are far more vigorous.<sup>3</sup> Chain cleavage also was noted earlier in the reactions of alkylamines with II.<sup>5</sup> These observations may indicate an ability of amino polymers, such as III, to tautomerize to a species more labile to nucleophilic cleavage (eq. 4) than are poly(aryloxyphosphazenes)(IV).



Treatment of chloro polymer II with a 20-fold molar excess of aniline gave a product having an intrinsic viscosity of 0.2 dl/g vs. 1.4 dl/g for IIIa prepared by the usual procedure, supporting the view that nucleophiles can cleave III possibly by the scheme shown in eq. 4. However, degradation of polyphosphazenes occurs under a variety of conditions, including the thermal depolymerization of poly(alkoxy-)<sup>1</sup>, poly(aryloxy-)<sup>1</sup>, and poly(alkylaminophosphazenes).<sup>4</sup> Also, the PN backbones of cyclooctachlorotetraphosphazene<sup>11</sup> and polydichlorophosphazene<sup>12</sup> apparently are reductively cleaved by thiolates.

The generally lower viscosities of polymers IIIh-k compared with those of IIIa-g (cf. Table I) probably are a consequence of the longer reaction times required for preparation of III h-k, which result in increased chain cleavage.

For comparison with the arylamino polymers III, the previously unreported copolymer VI and poly(alkylaminophosphazenes) VII and VIII were prepared (Table II). Non-geminally substituted poly(chlorodiethylamino-phosphazene) (V) was prepared by a modification of a procedure reported earlier (eq. 5).<sup>5</sup> Chloroamino polymer V does not react with aniline under conditions employed for the preparation of III, presumably because of steric hindrance by the diethylamino moiety to attack by aniline. The reaction did occur in boiling dioxane (eq. 5), but substitution was accompanied by extensive degradation ( $[\eta] = 0.13$  dl/g). The proton nmr spectrum of VI is consistent with the structure shown, although VI contains 2.18% residual chlorine.



Polymers VII and VIII (Table II) were prepared by a method similar to that for III. Poly[bis(benzylamino)phosphazene] (VII) decomposes at a lower temperature than do the arylamino polymers III, while poly[bis( $\beta$ -phenethylamino)phosphazene] (VIII) decomposes at a higher temperature (Table II). The glass transition temperature of the benzylamino polymer VII (75°C) is in the same range as those of III. This indicates, as mentioned above, that the presence of aryl groups in III contributes to their high glass transition temperatures, since VII is structurally a poly(alkylaminophosphazene), polymers which normally have glass transitions from -11° to 30°C.<sup>4,5</sup>

The intrinsic viscosities of VII and VIII (Table II) are comparable to but somewhat lower than many of the arylamino polymers. Greater chain degradation during the preparation of VII and VIII may be a consequence of the stronger nucleophilicity of benzylamine and  $\beta$ -phenethylamine compared with that of the arylamines.

The P-N stretching frequencies of VII and VIII (Table II) are consistent with other amino polymers, and their proton nmr spectra, though poorly resolved, are consistent with the structures shown.



## EXPERIMENTAL

### Materials

Hexachlorocyclotriphosphazene (I), purchased from El Monte Chemical was purified by recrystallization from heptane followed by vacuum distillation (130-140°C/20 mm), mp 110-112°C. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride prior to use, and benzene was predried by azeotropic distillation. Amines generally were distilled shortly before use. Glassware was oven-dried prior to each experiment, and all reactions were run under an argon flow. Proton nmr spectra were obtained using a Perkin-Elmer Model R32 90 MHz spectrometer, and infrared spectra were obtained with a Perkin-Elmer Model 187 spectrometer. Instruments used for thermal analyses are described in the footnotes to Table I. Elemental analyses were performed by Galbraith Labs, Knoxville, Tennessee.

### Polymerization of I and Isolation of II

Hexachlorocyclotriphosphazene (I, 50g) was polymerized at 240-245°C for 10-56 hr in evacuated sealed tubes.<sup>3</sup> In a dry box, containing an argon atmosphere, the polymerization mixture was taken up in dry benzene (~100 ml), and low molecular weight cyclics and oligomers then were separated from polymer II by coagulation of the polymer with n-pentane (~400 ml). Isolated II (17-43%) was immediately redissolved in benzene.

### Poly[bis(arylamino)phosphazenes] (III)

Poly[bis(phenylamino)phosphazene] (IIIa).<sup>4</sup> A solution of triethylamine (54.64g, 0.54 mol) and aniline (33.52g, 0.36 mol) was added dropwise to a stirred solution of polydichlorophosphazene (II, 13.85g, 0.12 mol). in 1:1 benzene-tetrahydrofuran (300 ml). Precipitate began forming almost immediately after addition was begun, the reaction was exothermic, and the reaction mixture became quite viscous (see below). After addition



was complete, the mixture was heated to reflux and allowed to stir for 48 hr. After the mixture had cooled to room temperature, it was filtered to remove triethylamine hydrochloride (23.0g, 70%) and the filtrate was added dropwise to several liters of methanol to precipitate the product. The polymer was washed with several portions of 1:1 methanol-water for several days to remove chloride ion (until the wash solution gave no precipitate with silver nitrate). The polymer then was taken up in THF, and the resulting solution was filtered and added dropwise to methanol to give, when dried, white IIIa (9.7g, 35%), which contained 0.76% residual chlorine.

During the preparation of a number of the arylamino polymers described in this report, the reaction mixtures became quite viscous after the addition of the amines. This increase in viscosity may result either from partially substituted polymer that is only sparingly soluble or from initial formation of some insoluble polymer hydrochloride salt that is later neutralized by triethylamine. In any case, frothing and scorching resulted if reflux temperatures were attained too quickly. Thus, in some cases (see below), mixtures were allowed to stir for several hours at room temperature or with gentle warming prior to heating to reflux. As the reactions proceeded, the viscosities of the mixtures decreased so that they were easily filtered after the reactions were complete.

Poly[bis(p-methylphenylamino)phosphazene] (IIIb). In a preparation similar to that of IIIa, p-toluidine (125.37g, 1.17 mol) in THF (130 ml) was added to II (15.10g, 0.13 mol) in 1:1 benzene-THF (200 ml). After 48 hr at reflux, precipitated p-toluidine hydrochloride (24.60g, 66%) was

removed by filtration and the filtrate was added to methanol as before to precipitate the product. The polymer was purified as described for IIIa to give white IIb (12.00g, 36%).

Anal. Calcd. for  $(C_{14}H_{16}N_3P)_n$ : C, 65.35; H, 6.28; Cl, 0.00; N, 16.33. Found: C, 64.43; H, 6.06; Cl, 0.90; N, 15.71.

In a similar experiment, a solution of p-toluidine (0.45 mol) and triethylamine (0.45 mol) was added to II in 2:1 THF-benzene. The mixture was stirred for 24 hr at room temperature, followed 57 hr at reflux; the longer reaction time was employed in an attempt to improve the analytical results for IIb. The product was isolated in 65% yield, but, because of the longer reaction time, gave an intrinsic viscosity of only 0.95 dl/g (compared with 1.3 dl/g for IIb prepared as described above).

Anal. Found: C, 63.49; H, 6.19; Cl, 0.66; N, 16.14.

Poly[bis(m-methylphenylamino)phosphazene] (IIc). In a preparation similar to that of IIIa, a solution of m-toluidine (66.43g, 0.62 mol) and triethylamine (62.74g, 0.62 mol) was added to II (18.07g, 0.16 mol) in 3:2 THF-benzene (250 ml). After 48 hr at reflux, precipitated triethylamine hydrochloride (24.4g, 55%) was removed, and the polymer was isolated and purified as described for IIIa to give white IIc (10.49g, 25%).

Anal. Calcd for  $(C_{14}H_{16}N_3P)_n$ : C, 65.35; H, 6.28; Cl, 0.00; N, 16.33. Found: C, 62.57; H, 6.27; Cl, 0.36; N, 16.00.

Poly[bis(o-methylphenylamino)phosphazene]. In a preparation similar to that of IIIa a solution of o-toluidine (68.5g, 0.64 mol) and triethylamine (64.6g, 0.64 mol) was added to II (18.65g, 0.16 mol) in 3:1 THF-benzene (350 ml). After 48 hr at reflux, precipitated triethylaminehydrochloride

(24.0g, 54%) was removed and the product was isolated and purified as described for IIIa to give cross-linked insoluble polymer (2.76g, 7%).

Anal. Calcd for: C, 65.35; H, 6.28; Cl, 0.00; N, 16.33.

Found: C, 53.39; H, 5.87; Cl, 4.85; N, 5.11.

Poly[bis(p-ethylphenylamino)phosphazene] (IIIId). In a preparation similar to that of IIIa, a solution of p-ethylaniline (66.7g, 0.55 mol) and triethylamine (55.5g, 0.55 mol) was added to II (13.00g, 0.11 mol) in 1.75:1 THF-benzene (275 ml). After 72 hr at reflux, triethylamine hydrochloride (44.5g, 147%) was removed, and the polymer was isolated and purified as described for IIIa to give white IIIId (22.85g, 73%).

Anal. Calcd for  $(C_{16}H_{20}H_3P)_n$ : C, 67.34; H, 7.08; Cl, 0.00; N, 14.73.

Found: C, 66.44; H, 6.93; Cl, 0.24; N, 14.66.

Poly[bis(m-ethylphenylamino)phosphazene] (IIIe). Polydichlorophosphazene (II, 6.55g, 0.056 mol) in benzene (60 ml) was added slowly to a stirred solution of m-ethylaniline (27.19g, 0.224 mol) and triethylamine (22.60g, 0.223 mol) in THF (100 ml). After stirring at room temperature overnight, the mixture was heated at reflux for 56 hr. After removal of triethylamine hydrochloride (11.68g, 76%), the polymer was isolated and purified as before for IIIa to give white IIIe (7.95g, 50%).

Anal. Calcd for  $(C_{16}H_{20}N_3P)_n$ : C, 67.34; H, 7.08; Cl, 0.00; N, 14.73.

Found: C, 64.52; H, 7.03; Cl, 0.65; N, 14.32.

Poly[bis(p-n-butylamino)phosphazene] (IIIIf). In a preparation similar to that of IIIa, a solution of p-n-butylaniline (110.5g, 0.74 mol) and triethylamine (74.8g, 0.74 mol) was added to II (17.20g, 0.15 mol) in benzene (120 ml) and THF (250 ml). The mixture was heated gently overnight

and then at reflux for 48 hr. Triethylamine hydrochloride (38.53g, 93%) was removed, and the polymer was isolated and purified as described for IIIa to give white IIIf (22.33g, 44%).

Anal. Calcd for  $(C_{20}H_{28}N_3P)_n$ : C, 70.34; H, 8.28; Cl, 0.00; N, 12.31. Found: C, 68.97; H, 8.18; Cl, 0.32; N, 12.29.

Poly[bis(p-methoxyphenylamino)phosphazene] (IIIg). In a preparation similar to that of IIIa, a solution of p-anisidine (61.8g, 0.50 mol) and triethylamine (55.5g, 0.55 mol) in THF (100 ml) was added to II (16.70g, 0.14 mol) in 2:1 benzene-THF (150 ml). After 48 hr at reflux, triethylamine hydrochloride (25.28g, 66%) was removed and the polymer was isolated and purified as described for IIIa to give light pink IIIg (16.59g, 41%).

Anal. Calcd for  $(C_{14}H_{16}N_3O_2P)_n$ : C, 58.12; H, 5.59; Cl, 0.00; N, 14.53. Found: C, 57.18; H, 5.69; Cl, 0.15; N, 14.31.

Poly[bis(m-methoxyphenylamino)phosphazene]. In a preparation similar to that of IIIa, m-anisidine (0.62 mol) and triethylamine (0.62 mol) were added to polymer II (0.12 mol). Removal of triethylamine hydrochloride (21.00g, 64%) after 56 hr of reflux and isolation and purification of the polymer as described for IIIa gave white product (1.60g, 5%) having an intrinsic viscosity of 0.55 dl/g;  $T_g = 78^\circ C$ ;  $T_d = 250^\circ C$ .

Anal. Calcd for  $(C_{14}H_{16}N_3O_2P)_n$ : C, 58.12; H, 5.59; Cl, 0.00; N, 14.53. Found: C, 54.37; H, 5.60; Cl, 0.96; N, 14.72.

Poly[bis(p-chlorophenylamino)phosphazene] (IIIh). A solution of p-chloroaniline (95.5g, 0.75 mol) and triethylamine (75.5g, 0.75 mol) in THF (200 ml) was added dropwise to II (21.71g, 0.19 mol) in benzene (125 ml).

Additional THF (50 ml) was added to the viscous mixture, and the temperature was raised slowly (over a period of 5 hr) to reflux. After 144 hr at reflux, triethylamine hydrochloride (24.67g, 47%) was removed by filtration and the filtrate was added dropwise to n-pentane (~3l). The precipitated product was taken up in THF, and the resulting solution was filtered and added dropwise to water to again precipitate the polymer, which was washed several days with several portions of water to remove chloride ion (until the wash water gave no precipitate with silver nitrate). The polymer again was taken up in THF and precipitated from water. Drying gave white IIIh (1.84g, 3%).

Anal. Calcd for  $(C_{12}H_{10}Cl_2N_3P)_n$ : C, 48.34; H, 3.39; Cl, 23.79; N, 14.10. Found: C, 46.80; H, 3.20; Cl, 21.96; N, 14.07.

In another experiment, reflux was maintained for only 48 hr. The product, isolated in 20% yield, gave an inherent viscosity of 0.8 dl/g.

Anal. Found: C, 40.44; H, 3.37; Cl, 22.54; N, 12.83.

Poly[bis(m-chlorophenylamino)phosphazene] (IIIi). Polydichloro-phosphazene (II, 21.00g, 0.18 mol) in benzene (90 ml) was added slowly to a stirred solution of m-chloroaniline (130.00g, 1.02 mol) and triethylamine (54.00g, 0.53 mol) in THF (300 ml). The mixture was heated at 60°C for 19 hr and then at reflux for 56 hr. Addition of the mixture to 1:1 methanol-water precipitated polymer, which was taken up in THF, filtered, and precipitated from n-pentane. The polymer was taken up in acetone and again precipitated from n-pentane, followed by washing for 24 hr with 3:1 water-methanol. Drying gave white IIIi (33.00g, 61%).

Anal. Calcd for  $(C_{12}H_{10}Cl_2N_3P)_n$ : C, 48.34; H, 3.39; Cl, 23.79; N, 14.10. Found: C, 45.69; H, 3.34; Cl, 23.30; N, 14.09.



Poly[bis(p-fluorophenylamino)phosphazene] (IIIj). In a preparation similar to that of IIIh, a solution of p-fluoroaniline (97.6g, 0.88 mol) and triethylamine (88.8g, 0.88 mol) was added to II (25.12g, 0.22 mol) in 2.5:1 THF-benzene (250 ml). After 24 hr of gentle heating and then 48 hr at reflux, triethylamine hydrochloride (47.0g, 78%) was removed and the polymer was isolated and purified as described for IIIh to give white IIIj (12.67g, 22%).

Anal. Calcd for  $(C_{12}H_{10}F_2N_3P)_n$ : C, 54.34; H, 3.81; Cl, 0.00; F, 14.33; N, 15.85. Found: C, 51.15; H, 4.06; Cl, 0.85; F, 12.40; N, 15.20.

Poly[bis(m-fluorophenylamino)phosphazene] (IIIk). In a preparation similar to that of IIIh, a solution of m-fluoroaniline (62.4g, 0.56 mol) and triethylamine (56.5g, 0.56 mol) was added to II (13.03g, 0.11 mol) in 2:1 THF-benzene. After 24 hr of gentle heating and 96 hr at vigorous reflux, triethylamine hydrochloride (21.6g, 71%) was removed, and the polymer was isolated and purified as described for IIIh to give white IIIk (8.09g, 28%).

Anal. Calcd for  $(C_{12}H_{10}F_2N_3P)_n$ : C, 54.34; H, 3.81; Cl, 0.00; F, 14.33; N, 15.85. Found: C, 51.70; H, 3.82; Cl, 1.09; F, 13.08; N, 15.95.

Poly[bis(m-trifluoromethylphenylamino)phosphazene]. In a preparation similar to that of IIIh, m-aminobenzotrifluoride (0.58 mol) and triethylamine (0.58 mol) were added to II (0.12 mol). Removal of triethylamine hydrochloride (19.55g, 59%) and isolation and purification of the product as described for IIIh, gave an off-white material (9.26g, 21%), having an inherent viscosity of 0.12 dl/g;  $T_g = 75^\circ C$ ;  $T_d = 199^\circ C$ .

Anal. Calcd for  $(C_{14}H_{10}F_6N_3P)_n$ : C, 46.03; H, 2.77; Cl, 0.00; F, 31.21; N, 11.51. Found: C, 42.36; H, 3.44; Cl, 1.31; F, 21.70; N, 12.88.



Poly(alkylaminophosphazenes) VI, VII, and VIII

Poly(diethylaminophenylaminophosphazene) (VI). A solution of diethylamine (65.70g, 0.90 mol) in benzene (100 ml) was added dropwise to a cooled (ice bath), stirred solution of II (10.66g, 0.09 mol) in benzene (150 ml). Diethylamine hydrochloride began precipitating almost immediately. After stirring at room temperature for 72 hr, the salt was removed by filtration, and the filtrate was added quickly (dropwise over a period of ~30 min) to acetone (~3l). The precipitated product was dried in vacuo at ambient temperature for 24 hr to give poly(diethylaminochlorophosphazene)<sup>5</sup> (V, 8.48g, 62%, 0.06 mol), which was taken up in benzene (150 ml). Dioxane was added to the resulting stirred solution, followed by dropwise addition of aniline (74.4g, 0.80 mol). The solution was heated at reflux for 48 hr. As the solution was allowed to cool to room temperature, aniline hydrochloride (3.0g, 39%) precipitated and was removed by filtration. The dark filtrate was added to methanol to give fine particles which were washed with methanol and then 1:1 methanol-water for several days. The product then was taken up in THF and precipitated from 3:1 methanol-water, which gave VI (2.98g, 24% based on V) as a white powder. The material contained 2.18% residual chlorine.

Poly[bis(benzylamino)phosphazene] (VII). Polydichlorophosphazene (9.10g, 0.08 mol) in benzene (100 ml) and THF (75 ml) was added slowly to a stirred solution of benzylamine (42.00g, 0.39 mol) and triethylamine (20.01g, 0.20 mol) in THF (250 ml). The solution was stirred at room temperature for 20 hr, followed by gentle heating for 7 hr. After standing overnight at room temperature, the reaction mixture separated into two layers. The bottom layer (60 ml, which contained only hydrochloride salt)

was discarded, and the top layer was added dropwise to methanol to precipitate the product, which was taken up in THF and precipitated from 1:1 methanol-water. The product then was washed first with water followed by methanol and dried to give white VII (15.00g, 73%).

Anal. Calcd for  $(C_{14}H_{16}N_3P)_n$ : C, 65.35; H, 6.28; Cl, 0.00; N, 16.33;  
Found: C, 62.96; H, 6.20; Cl, 0.24; N, 16.09.

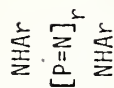
Poly[bis( $\beta$ -phenethylamino)phosphazene] (VIII). A solution of polydichlorophosphazene (II, 7.90g, 0.07 mol) in 1:1 THF-benzene (200 ml) was added slowly to a stirred solution of  $\beta$ -phenethylamine (51.0g, 0.42 mol) and triethylamine (42.4g, 0.42 mol) in THF (100 ml). The resulting viscous mixture was stirred overnight at room temperature. Additional THF (200 ml) was added, and the mixture was heated at 40°C for 4 hr. The product, which precipitated from the reaction mixture, was collected by filtration and washed first with methanol and then with water, and again with methanol. Drying gave VIII (9.4g, 47%) as white powder, which was soluble only in tetrachloroethane or hot chloroform. For an analytical sample, a portion of the material was taken up in hot chloroform, filtered by centrifugation, precipitated from methanol and dried.

Anal. Calcd for  $(C_{16}H_{20}N_3P)_n$ : C, 67.34; H, 7.08; Cl, 0.00; N, 14.73.  
Found: C, 67.92; H, 7.09; Cl, 0.24; N, 14.61.

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TABLE I



No.	Ar	Yield, % <sup>a</sup>	Tg, °C <sup>b</sup>	Td, °C <sup>c</sup>	Viscosity, dl/g	Infrared bands, P-N	cm <sup>-1</sup> P-N
IIIa	Ph	35	105	---	1.4 <sup>d</sup>	1170-1205	925-960
IIIb	p-MePh	36	97	250	1.3 <sup>d</sup>	1210	925-955
IIIc	m-MePh	25	76	262	1.4 <sup>d</sup>	1225	955
IIId	p-EtPh	73	88	245	0.7 <sup>d</sup>	1220	925-950
IIIe	m-EtPh	50	61	243	1.3 <sup>d</sup>	1220	940
IIIf	p-n-BuPh	44	53	253	0.9 <sup>d</sup>	1215	920-960
IIIg	p-MeOPh	41	92	266	1.3 <sup>d</sup>	1205	925-955
IIIh	p-ClPh	3	85	265	0.6 <sup>e</sup>	1180-1210	930-960
IIIi	m-ClPh	62	80	253	1.3 <sup>e</sup>	1205	950 (broad)
IIIj	p-FPh	22	---	260	0.7 <sup>e</sup>	1200	920-960
IIIk	m-FPh	28	80	249	0.3 <sup>e</sup>	1200	975

a Based on polydichlorophosphazene isolated from polymerization reaction.

b Values were determined at scan rates of 10°C/min by using the duPont 990 thermal analyzer with Cell Base Module II.

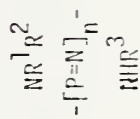
c Values were determined by using the duPont 951 thermogravimetric analyzer at heating rates of 20°C/min (static air), from extrapolated tangents to the linear regions above and below the change in slope in the trace of weight loss vs temperature.

d Intrinsic viscosity; obtained in THF at 25°C.

e Inherent viscosity; obtained in THF at 25°C; gave anomalous Huggins plot (see text).

TABLE II

Poly(alkylaminophosphazenes)

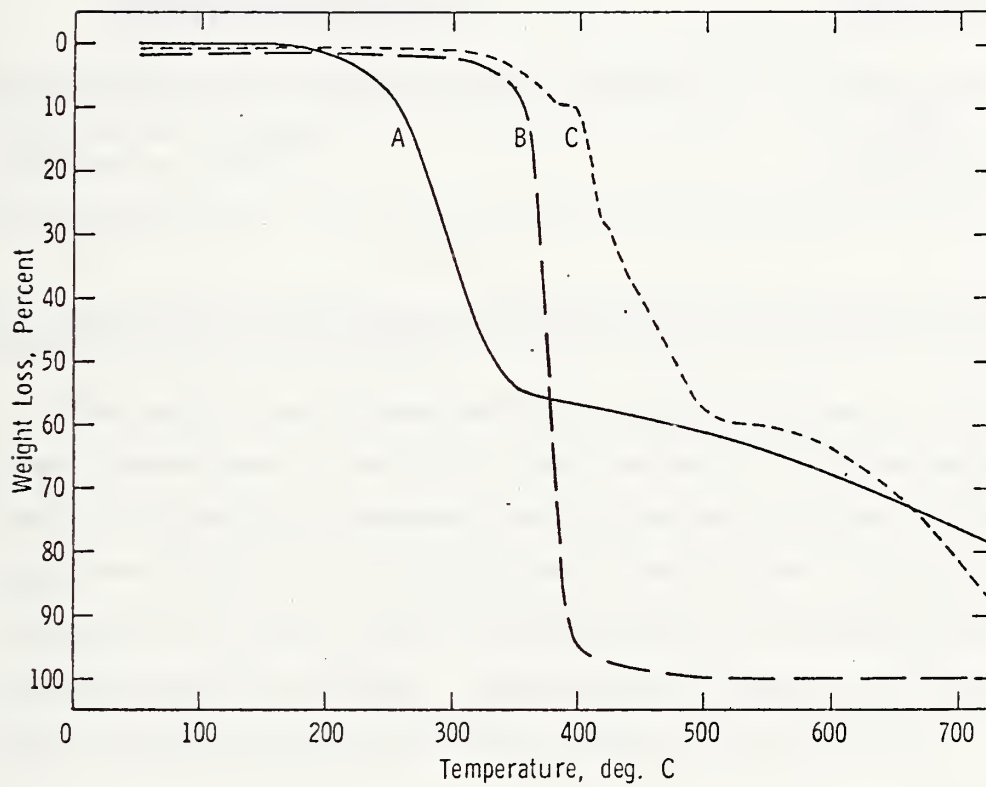


No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield, %	T <sub>g</sub> , °C <sup>c</sup>	T <sub>d</sub> , °C <sup>d</sup>	[η], dl/g	PN stretch. cm <sup>-1</sup>
VI	Et	Et	Ph	24 <sup>a</sup>	- - -	- - -	0.13 <sup>e</sup>	1210
VII	H	PhCH <sub>2</sub>	PhCH <sub>2</sub>	73 <sup>b</sup>	75	205	0.7 <sup>e</sup>	1240
VIII	H	PhCH <sub>2</sub> CH <sub>2</sub>	PhCH <sub>2</sub> CH <sub>2</sub>	47 <sup>b</sup>	- - -	280	0.7 <sup>f</sup>	1180

<sup>a</sup> Based on poly(diethylaminochlorophosphazene)(V) isolated (see text).<sup>b</sup> Based on polydichlorophosphazene (II) isolated from polymerization reaction.<sup>c</sup> Determined as described in footnotes of Table I.<sup>d</sup> Determined as described in footnotes of Table I.<sup>e</sup> Determined in THF at 25°C.<sup>f</sup> Determined in tetrachloroethane at 25°C.



Fig. 1. TGA curves for: (A) IIIb (static air); (B) poly[bis(trifluoroethoxy)phosphazene] (static air); (C) poly[bis(p-methylphenoxy)phosphazene] (oxygen).





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